

QUALITY ASSURANCE PROGRAM

Great Lakes Analytical
1380 Busch Parkway
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Signed

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1. INTRODUCTION

1.1 Quality Statement

Success in the environmental laboratory marketplace is dependent on three factors: quality, service, and price. Of these, quality is the fundamental factor. Quality is the foundation upon which the other two elements are based. If our clients do not have faith in the quality of our measurements then our product has no value to them. Price and service levels are irrelevant. Clearly, providing quality data to our clients must be the highest priority for the staff at Great Lakes Analytical. This commitment to quality starts with the top management of the laboratory. The President communicates this commitment to the analytical staff directly through staff meetings, interviews with new employees, and in the laboratories through daily interactions with the analytical staff. Indirectly, it is communicated to the analytical staff through the goals and objectives set by the President for his managers. Finally this commitment and specific quality criteria are communicated to the staff through this document, the Quality Assurance Program, and through method specific standard operating procedures. At Great Lakes Analytical, service may on occasion, be compromised in the pursuit of quality; but quality is never compromised in the pursuit of service. Our objective is to provide the highest quality data available in the laboratory marketplace, on time, and at an affordable price.

1.2 Definition

A Quality Assurance Program is an organization-wide network designed to assure that data produced within that network conforms to the highest standards set by state and/or federal regulations. The network functions at the management level through company goals and management policies; it functions at the analytical level through standard operating procedures and quality control. These two levels are spanned by data control and the reviewing process. The end result is a data package that is accurate, reproducible, and is presented in such a way as to be most useful to the client.

1.3 Scope

Great Lakes Analytical (GLA) analyzes thousands of environmental and industrial samples every month. Chemical and physical parameters must often be measured on the same sample. As such, the Quality Assurance Program must be able to accommodate the complications implicit in the analysis of many samples of widely varying matrices. Analytical methods employed at Great Lakes Analytical are those approved by the US EPA or state regulatory agencies whenever possible. Source documents for these methods include: the latest approved version of *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846; *Methods for the Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, March 1983; *Methods for the Determination of Organic Compounds in Drinking Water*, EPA-600/4-88/039, December 1988; CFR 40 136 Appendix A; *Standard Methods for the Examination of Water and Wastewater*, APHA, 18 ed. 1992; as well as other state and federal publications.

2. ORGANIZATION AND RESPONSIBILITY

Great Lakes Analytical has a structure to facilitate communications between the management and analytical levels. This structure ensures that the final data package produced for the client meets or exceeds regulatory standards. The following are brief descriptions of the major organizational levels (Figure 1 in Appendix).

2.1 President

The President reports directly to the Chief Executive Officer and the Board of Directors and is responsible for the overall financial, operational, and quality performance of the Corporation.

It is the responsibility of the President to ensure that the QAP is fully implemented at all times. The Quality Assurance Manager reports directly to the President and assists him in monitoring the implementation of the QAP. It is the responsibility of the Laboratory Manager to implement the QAP. The President mediates any conflicts that may arise in the interpretation of methods or the QAP between these two managers.

It is the responsibility of the President to ensure that the Chemical Hygiene Plan is fully implemented at all times and that a safe workplace and work practices are maintained. The Health and Safety Manager assists the President in this function.

The Vice President of East Coast operations also reports directly to the President.

2.2 Quality Assurance Manager

The Quality Assurance (QA Manager) is responsible for: overseeing and reviewing the Quality Assurance Program; all quality control procedures; internal checks and audits; QC data reporting; monitoring employee training; providing required QA/QC related training; and interfacing with the external auditors. The QA Manager updates the laboratory on changes to method requirements and procedures, and is responsible for controlling documentation of written procedures and audits.

The Quality Assurance Manager is also responsible for maintaining the laboratory's certifications and keeping abreast of changes in the programs in which the laboratory participates.

2.3 Health & Safety Manager

The Health and Safety Manager is responsible for overseeing the Health and Safety program. This includes routine internal health and safety audits of the facility as well as management of the Hazardous Waste Program. The Health and Safety Manager is also responsible for reviewing, revising, and providing training for the Chemical Hygiene Plan.

2.8 Analyst/Extraction Analyst

An analyst is responsible for all aspects of assigned analytical procedures, including overseeing sample preservation and preparation, performing the analysis, and reporting the results. Included in this is the adherence to all quality control procedures specified in the analytical methods or standard operating procedures and the full documentation of these procedures. The analyst has the responsibility and authority to stop analysis or withhold a result if quality control objectives are not met or resolved according to applicable standard operating procedures or their manager. In addition, the analyst is responsible for routine maintenance as well as documentation of that maintenance, of their equipment and for having sufficient supplies for analysis. Furthermore, each analyst is responsible for performing their job functions in compliance with the Chemical Hygiene Plan and for proper disposition or disposal of chemicals and samples.

2.9 Technician

The technicians are responsible for both laboratory and field support. Under the supervision of their manager, they are responsible for proper sample pick-ups, deliveries, and general laboratory support. In addition, they are responsible for bottle preparation in accordance with all quality control procedures and relevant standard operating procedures. Each Technician is responsible for performing their duties in compliance with the Chemical Hygiene Plan and for the proper disposition or disposal of chemicals and samples.

4. CLIENT COMPLAINTS

Client complaints can come to Great Lakes Analytical through various routes: Log-in personnel, Project Managers, the Client Services Manager, Marketing Associates, or the Laboratory Manager. It is the goal of Great Lakes Analytical to carefully listen to these issues and devise strategies that will prevent these problems from recurring.

When a complaint is received it is immediately brought to the attention of the Laboratory Manager. Support documentation is then assembled by the recipient of the complaint and evaluated by the Laboratory Manager the Client Services Manager or QA Manager. After a clear understanding of the problem has been reached, appropriate corrective actions are taken to resolve the client's complaint. These corrective actions are communicated to the client by the QA/Manager, Lab Manager,, Project Manager, CSM, President or other appropriate member of the staff.. The Laboratory Manager is responsible for implementation of the corrective action. The QA Manager will do an annual report summarizing these corrective actions and present it to the Laboratory Manager for review and further corrective actions if warranted.

5. SAMPLING

Sampling is an important part of any analysis. The result may be only as useful as the quality of the sampling effort. Great Lakes Analytical only performs limited sampling for it's clients, but does provide sampling containers and advises clients if requested of proper sampling procedures, containers and preservation techniques.

5.1 Sampling Containers and Preservation

Containers are purchased in large lots from various commercial sources and are equivalent in terms of construction materials and cleaning protocols, to those listed in "Specifications and Guidance for Contaminant-Free Sample Containers", EPA Document 93963316, December 1992. Containers are prepared in a designated area, labeled with the preservative added, affixed with a sample description label, and stored.

Samples brought to Great Lakes by clients who have done their own sampling, are checked for appropriate preservatives, corrected if possible, documented and stored upon arrival. Preparation of containers is done by technicians relying on Standard Operating Procedures for Bottle Preservation(Refer to the SOP for Receipt of Samples into the Laboratory). Sample containers are provided to clients with the appropriate preservatives as part of the analytical process. SOP's for drinking water sampling procedures are provided to clients who upon request .

6.4 Hazardous Samples

Hazardous samples are segregated from other samples and from each other by hazard class. These samples are Red-Tagged to identify them as hazardous to all possible handlers. The Red-Tag is a label, with a written description of the hazard, affixed to the sample container. Examples of the hazardous classes include Flammable, Asbestos, PCB's, Cyanides, and Acids. All hazardous samples are disposed of appropriately. Procedures and requirements for Red-Tagging samples are given in the SOP for the Handling of Hazardous Samples and the Chemical Hygiene Plan.

6.5 Sample Storage

Samples are kept in house for 4-6 weeks after analysis unless special arrangements have been made by the client. Storage areas are organized numerically in library fashion. Samples that do not require cold storage are maintained on shelving units. Refrigerated storage areas are maintained at 4 degrees Celsius. Samples are rotated out of the refrigerated storage and onto the shelving units after the originally requested analyses are completed. Daily temperature records are kept for every refrigeration unit.

Analysts and technicians retrieve the sample container allocated to their analysis from storage, analyze the sample, and return it to the shelf from which it originally came. After 6 weeks of storage, samples are removed from the shelves and disposed of appropriately, unless otherwise specified by the client. Records are kept of sample disposal dates.

6.6 Sample Shipping

In the event that Great Lakes needs to ship samples, the samples are placed in a cooler with enough ice to ensure the maintenance of 4 degrees C. The samples are carefully surrounded by packing to avoid breakage and a trip blank is enclosed for those samples to be analyzed for volatile organic compounds. The chain of custody is signed over to the courier and attached to the shipping paperwork. Samples are generally shipped overnight express or hand delivered by a Great Lakes Analytical courier to maintain sample integrity.

8. ANALYTICAL QUALITY CONTROL

Quality control measurements verify the integrity of the analytical results. While the goal of all quality control procedures remains constant, specific quality control procedures vary from method to method, and to some extent, with matrix type. Each analyst is responsible for a thorough understanding of the goals of the Quality Assurance Program, as well as how the program is implemented in each method. The analyst is also responsible for the documentation of all quality control measurements associated with a particular method. All records, reports and documentation are kept for a minimum of 5 years.

Great Lakes Analytical adheres to the quality control procedures set out in the latest approved version of *EPA SW-846* for the majority of analytical procedures. Great Lakes also adheres to any additional quality control procedures set out in a particular method. Other method references may include the Illinois Title 35, Wisconsin Department of Natural Resources NR 149, *Code of Federal Regulations* Title 40, and *Standard Methods*, 18th Edition, 1992.

8.1 Calibration

8.1.1 Calibration for Organic Analyses

EPA Method 8000B from *EPA SW-846*, is a general introduction to the quality control requirements for gas and liquid chromatography. It is followed by more specific methods developed for specific organic compounds. Great Lakes Analytical uses EPA Method 8000 and the specific EPA method to set-up the required quality control measures for each analysis. Standard operating procedures for the analytical methods and all quality control documentation measures are kept in the analysts' notebooks and reference binders.

The majority of organic instrumentation is calibrated with internal standards. Some instruments, because of the complex nature of the multi-peak chromatograms produced by the method, necessitate the use of external standard calibration. Surrogate compounds are included in the calibration processes for all organic analyses if applicable.

Initially, each instrument is calibrated for the method for which it is allocated. Once the operating parameters have been established according to the method, the analyst prepares standard solutions containing all the analytes of interest, any internal standards, and any surrogates that are appropriate for the method.

These standard solutions are prepared at different concentrations. One of the concentrations must be just above the detection limit and the others should define the linear range for the instrument. All of the standard solutions are prepared using Class A volumetric glassware and the highest quality solvents and stock standards commercially available. The number of standards prepared is determined by the requirements of the particular method. If there are no specific requirements then GLA will default to three standards.

The validity of the calibration curve must be checked daily for most instruments and more frequently for instruments with particularly sensitive detectors that tend to drift. The analyst prepares a daily calibration check standard solution in the same manner as the initial calibration standard solutions were prepared. The daily calibration check standard solution must be within 15% of the true value.

Some methods have prescribed limits set for the recoveries listed above that may be different. It should be noted that individual method specifications would override these general procedures. In addition, there may be calibration procedures prescribed in the method, such as GC/MS tuning with BFB or DFTPP, that are not described here in detail but are described in detail in the standard operating procedures for the method.

8.1.2 Calibration for Inorganic Analyses

EPA SW-846, *Standard Methods for the Examination of Water and Wastewater 18th Edition 1992*, and USEPA CLP Statement of Work for Inorganic Analysis ILM01.0 are the three source documents used by Great Lakes Analytical to develop the quality control measures for inorganic analyses.

GLA uses all three to develop minimum performance standards. Standard operating procedures for the analysis and the quality control documentation measures are kept in the analysts' notebooks and reference binders. The majority of inorganic instrumentation is calibrated with external standards. The calibration procedures are much the same for inorganic as they are for organic methods. Please refer to section 7.1.1 above. Because of the nature of the technology and greater volume of samples capable of being analyzed during a 24 hour period, inorganic calibration curves are checked on a more frequent basis.

8.2 Retention Time Windows

Most organic analyses use gas chromatography or liquid chromatography instrumentation. As the key to analyte identification in chromatography, retention time windows must be established for every analyte in a particular method on every column used for that method. These records are kept with the notebooks associated with an instrument for later identification and quantitation of the analytes.

Once the analyst has determined that the instrument is in optimum working order through calibration and calibration verification procedures, the analyst uses a mid-range calibration standard to establish the retention times of the individual analytes in a method. The analyst makes 3 injections of the same standard over a 72 hour period, tabulating the retention times for each analyte for each of the 3 injections. The standard deviation of the retention times is then calculated. The retention time window is defined as the average retention time from the daily check standard plus or minus 3 Standard Deviations.

Reporting Limit (RL) - the Reporting limit is a tool used by the laboratory to establish a criteria based on laboratory experience or specific client needs. RL's are always established at or above the MDL but may or may not be above the PQL. RL's are generally set by client Data Quality Objectives (DQO) or the lowest reproducible standard in the calibration curve.

8.5 Instrument Maintenance

Great Lakes Analytical is dedicated to providing our clients with state-of-the-art technology. Instrumentation is purchased with sensitivity, accuracy, efficiency, and dependability as criteria. All instruments have log books in which calibrations, adjustments, routine maintenance, and any repairs are recorded. Calibrations, routine maintenance, and adjustments are part of the analysts' responsibilities. Service contracts are in place for some of the instruments for any major repairs. The highest quality gases, reagents and spare parts are kept on hand to minimize repair time and optimize instrument performance.

Each entry in the instrument log book includes the date, the analyst, a detailed description of the problem, a detailed explanation of the solution, and a verification that the instrument is functioning properly. In addition, standard operation procedures for organic methods specify and require documentation of routine maintenance procedures like changing of septa in injection ports, changing of gas tanks, and cleaning of detectors.

8.6 Control Limits

The analytical process is controlled not only by instrument calibration as discussed above but by quality control measurements of the labor intensive portions of the analysis as well. These involve measurements of method blanks, accuracy and precision. Before any analytical batch is analyzed, a check standard and reagent blank are analyzed to verify that the method is in control. The quality control samples are analyzed to determine the quality of the analytical process. All QC must pass for data to meet final approval.

8.6.1 Method Blank

The method blank must be free of contamination to determine that the extraction or preparation batch was free from contamination from an outside source and to prevent the overestimation of contaminants in the environmental samples.

With the exception of a few compounds for a few analyses, the method blank should quantitate to a value of less than half the PQL (or reported detection limit) for the analytes of interest. The exceptions are enumerated in the specific standard operating procedures.

Monday: 10 soil samples are received for analysis. A Blank, LCS, Matrix Spike and Matrix Spike Duplicate are run with the Daily Batch and reported.

Wednesday: 10 more soil samples are received for analysis. A Blank and LCS are run with this Daily batch and reported along with the Matrix Spike and Matrix Spike Duplicate from Monday. This Virtual Batch is complete because it contains 20 samples within the seven day period.

Precision data may be generated for matrix or blank samples, however, the matrix sample is preferred because it better approximates the performance of the method on real world samples. In the case of ground water and waste water samples a separate sample volume is not often provided for matrix spiking. In these situations the frequency will be blank spike and duplicate every Virtual Batch or 20 samples, but not less than once a week, with a blank and LCS analyzed with each consecutive batch during that week. Both the matrix spike (MS) and the matrix spike duplicate (MSD) are analyzed in the same manner as rest of the analytical batch. The relative percent difference between the two spiked duplicates is calculated and documented (Figure 5 in Appendix). The relative percent difference is calculated as follows (reported as the absolute value):

$$\text{Relative \% difference} = \frac{\text{Conc. of MS} - \text{Conc. of MSD}}{(\text{Conc. of MS} + \text{Conc. of MSD})/2} \times 100$$

The relative percent difference for a particular analyte must fall within the control limit established for that analyte. For the procedure for establishing control limit see section 8.6.5.1.

8.6.3.2 Exceptions to Precision General Procedure

Specific projects or regulatory agencies may require precision measurements more stringent than those described above. In such cases the laboratory will operate at the higher level of quality assurance required. In no case will the laboratory perform at a level lower than that described in the general procedure.

8.6.4 Surrogates

In most organic analyses surrogate compounds are spiked into all environmental and quality control samples. They act as a secondary check on method performance in that they must meet established acceptable recovery limits. These limits define the minimum and maximum recoveries that must be obtained for the particular environmental matrix. Limits are set semi-annually based on 15 - 20 consecutive data points per each matrix. Data points used to determine the control limits are evaluated using a statistical out-liers test.

Samples that fail to meet the limits are evaluated to determine the cause of the result. If no acceptable reason can be found the samples are re-extracted and reanalyzed. If the data is still outside of the acceptable limits the data is appropriately flagged.

8.7 Materials

Material purchased for use in the analytical process are all of the an acceptable purity or quality commercially available for the intended purpose. This includes all gases used in gas chromatography, all solvents, acids, and bases used in extraction or digestion, dilution, and standard preparation, stock standards, and any other routinely restocked items.

8.8 Cleaning Procedures

The following is the general cleaning procedures used for most analytical glassware at Great Lakes Analytical.

1. Rinse with hot tap water.
2. Scrub with detergent.
3. Rinse 3 times with hot tap water.
4. Rinse 3 times with deionized water.
5. Air dry and store.

Specific EPA methods require procedures that may vary from the cleaning procedures listed above. These specific standard operating procedures are posted in the glassware cleaning area and are kept on record with the appropriate analysts and the Quality Assurance Manager.

10. INTERNAL QUALITY CONTROL CHECKS

Great Lakes Analytical utilizes five different organizations to participate in eight Performance Evaluation programs. All are single blind and scheduled throughout the year. The list of programs is as follows:

<u>Organization</u>	<u>Program</u>	<u>Analysis Sets</u>
<u>Annually</u>		
Environmental Research Associates	Real World Matrix	2
Environmental Research Associates	Drinking Water	4
New York Dept. of Health	Non-Potable Water	2
New York Dept. of Health	Potable Water	2
EPA Water Supply	Drinking Water	2
EPA Water Pollution	Waste Water	2
Wisconsin DNR	Env. Ref. Sample Program	1
ELPAT	Lead in Paint Chips, Soils, Wipes and Air	4

Clients are encouraged to submit quality control samples to Great Lakes and on request, arrangements will be made to split samples and subcontract to another laboratory as a confirmatory check.

In addition, a stock of performance evaluation samples are kept to be administered blind to the analyst at the discretion of the QA Manager for more frequent internal performance checks.

11. INTERNAL AUDITS

Performance audits are done every quarter for every analyst. The audit responsibility can be divided between the QA Manager and the Department Manager, with each performing the audits. Audit forms have been designed for each analysis type to focus on the important documentation and procedural steps.

The auditors review the analyst's notebook for documentation of all quality control measurements, their frequency, and the clarity of the documentation. The notebook must be useful to any person who wishes to inspect the history of the analysis. Analysts must also have equipment logs, repair manuals, and adequate tools to keep instruments calibrated. The analyst's data reporting procedures are also reviewed to ensure that results can be easily traced to a notebook. The results of a system audit are discussed with the Department Manager, who will then review the findings with the appropriate analyst(s) and kept on file. If any discrepancies are noted, corrective actions are initiated.

Periodically following each audit, the QA Manager and Department Manager hold a meeting to review audit deficiencies and the progress of corrective actions. Annually the QA Manager and Lab Manager review the audit findings and implement any additional changes necessary to improve the quality system.

12.1.7. For more complex and long bench time tests it is not uncommon for multiple analysts to work on a single batch or page. This may involve analysts on the same shift or a shift to shift continuation of the analytical process. Many of the preprinted log books incorporate spaces for multiple analysts initials at various stages in the analytical process. Anytime an entry is made by an analyst other than the "signing" analyst it will be accompanied by the analyst's initials and date of the entry.

12.1.8. Completed lab note books are to be labeled with the date of the last entry and turned in to the QA Manager. Any unused pages will be "Z'd" out.

12.1.9. Log books will be archived for 5 years.

12.2 Data Review

Data travels through several processes before the final data package is released to the client. The path from the instrument response to the final report begins with the documentation of all testing parameters in the analyst's notebook.

Examples for all sample calculations as well as the quality control measurements are documented in the notebook or SOP for the specific method. Review of the analysis data, from the original data to the result reported, is completed by a peer or department manager.

The analysts are responsible for transferring the data to a set of laboratory worksheets. The worksheets are generated specific to the client's requests on the chain of custody. When completed the worksheets are submitted to the Project Manager for review.

At a minimum the standard laboratory report shall contain the following information:

- Client name and address
- Client project manager or contact
- Client sample identification and project name or number
- Laboratory sample number
- Date sampled
- Date received
- Date extracted or digested (if applicable)
- Date analyzed
- Method of analysis including EPA method code (if applicable)
- Practical Quantitation Limit or Reporting Limit
- Method Detection Limit (if required)
- Sample results
- Definition of ND
- Elevated detection limit statement if sample was reported at a dilution
- QC data consisting of Surrogate, LCS and MS/MSD recoveries and control limits

13. TRAINING

When reporting for work for the first time, all new employees receive a copy of the Personnel Policy Manual, and if appropriate for their job function the Chemical Hygiene Plan, and a copy of the Quality Assurance Program manual. These are his or hers to keep as part of his or her reference materials. The sole responsibility of the new employee is to read and understand the contents of these manuals. Once the new employee has read and understood the contents of the manual, he or she must sign a document that states that he or she agrees to *adhere to the requirements prescribed* therein. Additionally the new employee will receive appropriate training on one or more of these documents (See the SOP for Employee Training for further details concerning both new employee and ongoing employee training programs). These records are kept on file with the QA Manager. Only then does further on the job training take place.

The Personnel Policy Manual contains information about the company's history and objectives, administrative scheduling, benefits, and general administrative policies.

The Chemical Hygiene Plan contains pertinent information about the chemicals to which employees may be exposed and how to properly interact with those chemicals, preventative procedures to avoid emergencies as well as procedures to cope with emergencies like spills, injuries and fire.

The Quality Assurance Program manual contains information about the goals of the Quality Assurance Program and their implementation.

Each new analyst reviews reference binders that includes copies of the SOP's and source methods for which he or she will be held responsible, all related extraction, cleanup, and dilution methods, analytical standard operating procedures, all relevant quality control documentation forms, standard operating procedures for filling out those forms, and procedures for troubleshooting and corrective action.

Additional verbal instruction from both the previous analyst and a quality assurance staff member is provided to ensure a thorough understanding of the requirements set out by the Quality Assurance Program Manual and the analytical methods. The previous analyst then introduces the new analyst to all the instrumentation involved in his or her analyses. Standard operating procedures, preventative maintenance, and troubleshooting for the instrument are reviewed by both the previous and new analyst. The maintenance logbook is explained and any history specific to an instrument is reviewed by the previous and the new analyst. (Refer to the SOP for Employee Training)

GC/MS-2

Installed 11/91

Hewlett-Packard 5971 Mass Selective Detector
Hewlett-Packard 5890 II Gas Chromatograph
J&W DB5MS 0.32 mm X 30M Column for EPA Method 625, 8270
Hewlett-Packard 7673A Auto-sampler
MS-DOS Instrumentation Control Software
Hewlett-Packard Chemstation and Enviroquant Target Data Management System

GC/MS-3

Installed 5/94

Hewlett-Packard 5972 Mass Selective Detector
Hewlett-Packard 5890 II Gas Chromatograph
J&W DB 624 0.53 mm X 75 M Column for EPA methods 624, 8260
Tekmar LSC 3000 Purge and Trap
ALS 2016 Auto-Sampler & Auto-Sampler Heater
MS-DOS Instrumentation Control Software
Hewlett-Packard Chemstation and Enviroquant Target Data Management System

14.1.2 Gas Chromatographs

GC-1

Installed 8/90

Hewlett-Packard 5890 II Gas Chromatograph
Restek RTX-502.2 105 M Column for EPA 502.2, 8021, 601, and 602
OI Corp. ELCD/PID Detectors
MS-DOS Instrumentation Control Software
Hewlett-Packard Chemstation and Enviroquant Target Data Management System
Tekmar LSC 2000 Purge and Trap
Tekmar ALS 2016 Auto-sampler

GC-2

Installed 12/90

Hewlett-Packard 5890 II Gas Chromatograph
J&W DB5 608 30 M X 0.53 mm column for Methods 8080 and 8150
ECD/ECD Detectors
MS-DOS Instrumentation Control Software
Hewlett-Packard Chemstation and Enviroquant Target Data Management System
Hewlett-Packard 7673A Auto-sampler

GC-8
Hewlett-Packard 5890 II Gas Chromatograph
J&W DB-VRX105 M X 0.53 mm column for EPA 8021, 601 and 602
OI Corp. ELCD/PID Detectors
MS-DOS Instrumentation Control Software
Hewlett-Packard Chemstation and Enviroquant Target Data Management System
Tekmar ALS 2016 Autosampler
Tekmar LSC 2000 Purge and Trap

Installed 6/96

GC-9
Hewlett-Packard 5890 II Gas Chromatograph
2 DB-608 0.53 mm X 30 M columns for EPA 8150, 8080
ECD/ECD Detectors
MS-DOS Instrumentation Control Software
Hewlett-Packard Chemstation and Enviroquant Target Data Management System
Hewlett-Packard 7673A Auto-sampler

Installed 10/93

GC-10
Hewlett-Packard 5890 II Gas Chromatograph
2 RTX5 30M X 0.53 mm columns for WDNR DRO and TPH-Diesel
FID/FID Detectors
Hewlett-Packard 7673A Autosampler
Hewlett-Packard 3396 II Integrator
MS-DOS Instrumentation Control Software
Hewlett-Packard Chemstation and Enviroquant Target Data Management System

Installed 6/94

GC-11
Hewlett-Packard 5890 II Gas Chromatograph
J&W DB-624 0.53 mm X 60 M column for EPA 8020, TPH-Gas, GRO/PVOC
FID/PID Detectors
Tekmar LSC 2000 Purge and Trap
Tekmar ALS 2016 Autosampler
Hewlett-Packard 3392A Integrator

Installed 8/95

GC-12
Hewlett-Packard 5890 Gas Chromatograph
2 DB-5 30M X 0.32 mm columns for EPA 8150, 8080
ECD/ECD Detectors
Hewlett-Packard 7673A Autosampler
MS-DOS Instrumentation Control Software
Hewlett-Packard Chemstation and Enviroquant Target Data Management System

Installed 8/95

14.2 Inorganic Analytical Instrumentation

14.2.1 Trace Metal Analytical Instrumentation (AA and ICP)

Varian Liberty 100 ICP Optical Emissions Spectrometer Installed 9/92
SPS-5 Auto-sampler
GRID 386 Model MFP 320 Data Acquisition System

Varian SpectrAA-600.DBQ Atomic Absorption Spectrophotometer Installed 6/94
Varian VGA 77 Hydride Generator
IBM OS/2 Operating System
Panasonic KX-P1150 Printer

Varian SpectrAA-600z Atomic Absorption Spectrophotometer Installed 6/94
Zeeman Graphite Tube Atomizer-100
Varian PSD97Z Programmable sampling system
IBM OS/2 Operating System
Panasonic KX-P1150 Printer

14.2.2 General Chemistry Analytical Instrumentation

Barnstead E-Pure Water Purification System

Blue M- Stable Therm Gravity Oven

American Scientific Products- DX-68 Drying Ovens

Ney- Model 525 Series II Muffle Furnace

Milton Roy Spectronic 21 UV/Visible Spectrophotometer

Mettler AT-250 Analytical Balance

Parr- Model 1108 Oxygen Bomb

Pensky-Martens Closed Cup Flash Point Tester

Cleveland Open Cup Flash Point Tester

YSI Model 35 Conductivity Meter

Fisher 925 pH/Ion meter

A10 Tekmar Laboratory Mill

14.4 Field Sampling Equipment

Isco 2910 Composite Sampler (2)

14.5 Sample Storage

Freezer Storage: Approximately 60 cubic feet in 4 separate, lockable, and temperature-monitored freezers.

Refrigerated Storage: Approximately 231 cubic feet in 7 separate and temperature-monitored refrigerators.

Unrefrigerated Sample Storage: Approximately 393 square feet of shelving for sample storage

BLANK DEFINITIONS:

Calibration Blank-

An organic or aqueous solution that is as free of analytes as possible and prepared with the same volume of reagents used in the preparation of calibration standards. The calibration blank is used to give the null reading for the instrument response versus concentration calibration curve.

Equipment Blank-

An organic-free aqueous solution that is opened in the field, poured appropriately over and through the sample collection device, collected in a sample container and returned to the lab as a sample. Equipment blanks are a check of sampling device cleanliness.

Field Blank-

An organic-free aqueous solution that is transferred from one preserved vessel to another at the sampling site. This serves as a check on reagent and environmental contamination.

Method Blank-

An organic or aqueous solution that is as free of analyte as possible and contains all the reagents in the same volume as used in the processing of the environmental samples. The reagent blank is carried through the complete preparation procedure and is used to correct for possible extraction procedure contamination.

Trip Blank-

An organic-free aqueous solution that is transported to the sampling site and returned to the laboratory without being opened to serve as a check on contamination originating from sample transport, shipping and site conditions.

COMPARABILITY:

An expression of confidence with which one data set can be related to another.

DATA QUALITY:

The totality of features and characteristics of data that bears on its ability to satisfy a given purpose. The characteristics of major importance are accuracy, precision, completeness, representative results and comparability.

QUALITY ASSURANCE:

The total integrated program for assuring the reliability of laboratory data including quality planning, quality assessment and quality improvement efforts to meet user requirements at an economical level. Quality Assurance incorporates procedures for field sampling, sample handling and storage, analytical quality control and document preparation and review.

QUALITY ASSURANCE PROJECT PLAN:

The orderly assembly of detailed and specific procedures by which the laboratory defines how it produces quality data for a specific project or method. The laboratory has one Quality Assurance Program but multiple Quality Assurance Project Plans for various analytical projects.

QUALITY CONTROL:

The routine application of procedures such as blanks, spikes and spike duplicates for obtaining prescribed standards of performance in the measurement process.

RCRA:

The Resource Conservation and Recovery Act.

REAGENT GRADE:

Analytical Reagent (AR) Grade, ACS Reagent Grade and Reagent Grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REPRESENTATIVE RESULTS:

The degree to which data accurately and precisely represents a characteristic population, parameter variations of a sampling point or an environmental condition.

SAMPLE:

A discreet representative part or a single item from a larger group presented to the laboratory for analysis.

DUPLICATE SAMPLE:

Two replicate aliquots taken from the same source for which determination of composition or contamination is requested or required.

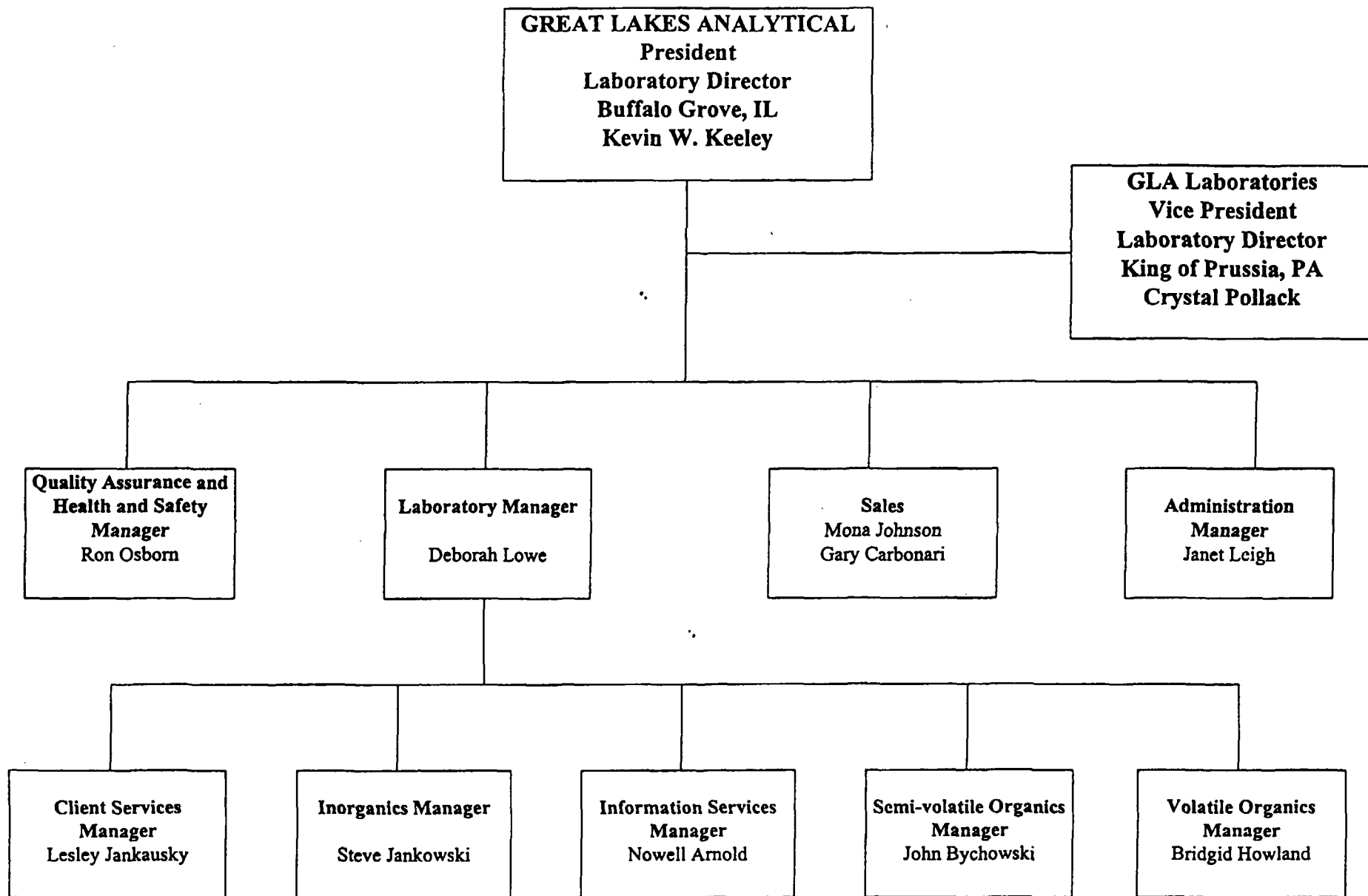
WATER:

A reference to Reagent, Analyte-Free, Laboratory Pure or ASTM Type II water means any distilled or deionized water which is free of contaminants that may interfere with the analytical test.

GENERAL CHEMISTRY

Acidity	305.1
Alkalinity	310.1
Biochemical Oxygen Demand	405.1/SM 5210.B
Chemical Oxygen Demand	410.4
Chloride	325.3
Chlorine Demand	409
Chlorine Residual	330.3
Color	ASTM04979-89
Cyanide	9012/335.4
Fluoride	340.2
Cyanide Amenable to Chlorination	9012/335.4
Ignitability - Flash Point Closed Cup	ASTMD93-85
Ignitability - Flash Point Open Cup	ASTMD92-85
Hardness	130.2
Ammonia	350.1
Nitrite	353.2
Nitrate	353.2
Total Kjeldahl Nitrogen	351.2
Odor	ASTMd4979-89
Oil & Grease - Liquid	413.3 / 1664
Oil & Grease - Solid	5520
Oxygen (dissolved)	360.1
Paint Filter test	9095
pH (corrosivity) - Liquid	9040A
pH (corrosivity) - Solid	9045B
pH (corrosivity) - pH paper	9041A
Phenolics (total colorimetric)	9065/420.4
Phenolics (low level detection)	9065
Phosphate (ortho) / Phosphorus	365.2
Reactivity with Acid, Base, Water	SW-846 7.3.2
Reactive Cyanide	SW-846 7.3.3
Reactive Sulfide	SW-846 7.3.4
Specific Gravity	ASTMD1429-86
Ash Content	160.4
Dissolved Solids (filterable)	160.2
Total Solids	160.3
Volatile Solids	160.4
Sulfide	9030/376.1
Sulfate	375.2
Total Organic Halogens (TOX)	9020B
Total Petroleum Hydrocarbons	418.1
Turbidity	180.1

ORGANIZATIONAL CHART



Client ID
Project ID QC TEST

QC Batch METP 1045 (548)
Original
Matrix Soil

Prep Method SW-846 3050A
Prep Date 06/27/97 10:28
Analysis Method SW-846 7421

QC results affect the following production samples:

1527

QC results for Method Blank [1528]

Run Instrument: VARIAN G.F. Spectra A 600

Parameter	Analyzed	Result	RDL	Units
Lead	06/27/97	ND	0.25	mg/kg

Project Manager

Client ID
Project ID QC TEST

QC Batch METP 1045 (548)
Original 1527
Matrix Soil

Prep Method SW-846 3050A
Prep Date 06/27/97 10:28
Analysis Method SW-846 7421

QC results affect the following production samples:

1527

QC results for Matrix Spike [1530] - Matrix Spike Duplicate [1531]

Parameter		Original Result	QC Result	Pct Recov	MS/MSD Limits	RPD Limits	Spiked Amount	Analyzed	Instru ID
Lead	MS	ND	50	100	72-116		50mg/kg	06/27/97	GFAA
	MSD		50	100		0 0-20	50mg/kg	06/27/97	GFAA

Project Manager

October 29, 1998
Carlson Environmental, Inc.
Attn: Margaret Karolyi
312 West Randolph Street
Chicago, IL 60606

Dear Margaret:

Below are Great Lakes Analytical's responses to US EPA comments included in your August 17 transmittal:

50. Section 4.2, Item 1, Page 8: An SOP for the preparation of bottles for EPA Method 5035 is attached.
56. Section 5.2, Laboratory Equipment, Page 17: Calibration procedures for the analytical methods are found in the included SOPs.
58. Section 7.0, ANALYTICAL SERVICES, Page 17-18: The following SOPs are enclosed:
- The Determination of Mercury in Liquids and Solids, GLA 245.1.5 BG, Rev. 2.0
 - The Determination of Total Cyanide and Cyanide Amenable to Chlorination in Liquids and Solids, GLA 335.4 BG, Rev. 2.0
 - The Digestion of Liquids for the Analysis of Metals, GLA 3015 BG, Rev. 3.0
 - The Digestion of Solids for Analysis of Metals, GLA 3050 BG, Rev. 3.0
 - Analysis of Metals Using ICP, GLA 6010 BG, Rev. 2.0
 - Analysis of Metals Using GFAA, GLA 7000 BG, Rev. 2.0
 - Organic Extraction and Sample Preparation for Semivolatile Determinative Methods, GLA 3500 BG, Rev. 1.1
 - Polychlorinated Biphenyls by Gas Chromatography: Capillary Column Method, GLA 8082 BG, Rev. 1.0
 - The Determination of Volatile Organic Compounds by Purge and Trap and Gas Chromatography Mass Spectrometry GLA 8260 BG, Rev. 2.0
 - Polynuclear Aromatic Hydrocarbons by HPLC, GLA 8310 BG, Rev. 1.1
59. Section 7.0, ANALYTICAL SERVICES, Page 17-18: Method performance studies for Tantalum will follow
62. Section 8.2, Laboratory Quality Control Checks, Page 18-19: A description of corrective actions for laboratory out of control events can be found in Section 6.0 of the attached SOPs.
63. Section 8.2, Laboratory Quality Control Checks, Page 19, last bullet: Section 6.6 of Polychlorinated Biphenyls by Gas Chromatography: Capillary Column Method, GLA 8082 BG, Rev. 1.0 addresses confirmation procedures to be employed. As detailed in this section, the laboratory will report the higher of the two results when there is significant difference between the two measurements.
64. Section 9.1, Field Data, Page 19: Not applicable to Great Lakes Analytical
65. Section 9.2, Laboratory Data, Page 20: Project Reporting Limits have been transmitted to CEI.
71. Section 5.1, Sample Containers and Preservation, Page 11: Enclosed is a copy of our SOP for the Preparation of Sample Containers for EPA 5035.

72. Section 6.3, Sample Log-in, Page 12: Sample Chain of Custody will be maintained and documented prior to receipt at the laboratory. Great Lakes Analytical maintains a secure laboratory facility. Access is restricted and limited to employees and authorized visitors. Custody of samples within the laboratory is well documented in the log books, bench sheets and run logs maintained by our Chemists and Technicians.
73. Section 6.3, Sample Storage, Page 13: After sample log-in, samples for Volatile Organic analysis are stored in the Volatile Organics Department separate from samples for other types of analysis as well as standards and extracts.
74. Section 8.0, Analytical Quality Control, Page 15-23: A table listing MDLs, PQLs and RLs was transmitted previously. Tables with accuracy control limits and surrogate control limits are enclosed.

Sincerely,

GREAT LAKES ANALYTICAL

Kevin W. Keeley
President/Laboratory Director

May 28, 1999

Margaret Karolyi
Carlson Environmental, Inc.
65 East Wacker Place
Suite 1500
Chicago, Illinois 60601

Dear Ms. Karolyi,

Enclosed is the response to the EPA's comments on Great Lakes Analytical's standard operating procedures (SOPs) and performance data. The following outlines the actions taken to fulfill their requests:

General Comments

- SOPs are included for Pesticides, SPLP, pH, and TOC. Please note that SOP GLA 160.1/4 BG contains the procedure for TOC by ASTM Method D2974-87 and the procedure for determining percent dry weight.

I. Control Limits

- A. The control limits for SPLP Pb are 78 – 114 % recovery for the LCS, and 77 – 113 % recovery for matrix spikes.
- B. MDLs, PQLs, and RLs for VOCs, Pesticides, PNAs and PCBs are included in tables and are attached to the back of each SOP. Please note that the Action Level tables in the October 1998 SIWP do not reflect the correct reporting limits for some of the target analytes. Use the table submitted here as guidance for reporting limits.

II. Mercury SOP GLA 245.1/5 BG

- A. MSA has been added to the SOP (Section 11.6.5).
- B. The laboratory has always ended each analytical run with a calibration blank and check standard. The SOP has been revised to include this step in the procedure (Section 11.6.3).
- C. The equations for %Rec and RPD calculations have been added (Sections 11.7.3 and 11.7.4).

III. Total Cyanide SOP GLA335.4 BG

- A. MSA has been added to the SOP (Section 6.7).
- B. The laboratory has always ended each analytical run with a calibration blank and check standard. The SOP has been revised to include this step in the procedure (Section 11.7.5).
- C. The equations for %Rec and RPD calculations have been added (Sections 11.8.4 and 11.8.5).

IV. Digestion of Liquids SOP GLA 3050 BG

- A. Tantalum (Ta) is going to be analyzed by one of our network laboratories, Sequoia Analytical in Walnut Creek, California. A copy of their SOP for liquid digestions is included (SOP 018).

- B. A table has been added to the SOP (Appendix B) that specifies the components of each standard solution.

V. Digestion of Solids SOP GLA 3050 BG

- A. Tantalum (Ta) is going to be analyzed by one of our network laboratories, Sequoia Analytical in Walnut Creek, California. A copy of their SOP for solids digestions is included (SOP 018a).
- B. Discussion of the preparation of the LCS and a reference to the % dry weight determination has been included (Section 11.3).
- C. Silver (Ag) has been added to Section 11.4.
- D. A table has been added to the SOP (Appendix B) that specifies the components of each standard solution.

VI. Metals by Graphite Furnace SOP GLA 7000 BG

- A. The concentrations of the calibration standards has been added (Section 11.2.1)
- B. The recommended instrument parameters have been added (Section 11.1).
- C. MSA has been added to the SOP (Section 11.3.5).
- D. The equations for %Rec and RPD calculations have been added (Sections 11.4.3 and 11.4.4).

VII. Metals by ICP SOP GLA 6010 BG

- A. MSA has been added to the SOP (Section 11.4.8).
- B. The laboratory has always ended each analytical run with a calibration blank and check standard. The SOP has been revised to include this step in the procedure (Section 11.4.7).
- C. The equations for %Rec and RPD calculations have been added (Sections 11.5.3 and 11.5.4).

Note: A copy of Sequoia Analytical's ICP SOP has been included for the analysis of Ta.

VIII. Organic Extractions SOP GLA 3500 BG

- A. The determination of % dry weight has been referenced in the SOP (Section 13.3.12).
- B. The laboratory does obtain adequate performance using methylene chloride as the extraction solvent for solids. However, a mixture of acetone/methylene chloride is used when extracting solid sample for pesticides and PCBs.
- C. The laboratory does obtain adequate performance with a final extract volume of 10 ml for Method 8310 (refer to the MDL table at the back of SOP GLA 8310BG).

IX. PCBs by GC SOP GLA 8082 BG

- A. Each analytical run ends with a check standard. This has been added to the SOP (Section 6.3).
- B. Surrogate standards are now prepared in acetone. This has been changed in the SOP (Section 10.1.1).
- C. The concentrations of the calibration standards has been added (Section 8.1).

- D. The confirmation analysis of PCBs follows the same stringent calibration and QC requirements as the primary analysis (See Section 6.6).
- E. The equations for %Rec and RPD calculations have been added (Sections 11.5.5 and 11.5.6).
- F. The % dry weight has been added to the equation for calculating final results of solids (Section 11.5.3).
- G. The typo was fixed. Moreover, Section 11.5.4 has been added to discuss the reporting of detections above the MDL but below the RL.

X. Analysis of Volatiles SOP GLA 8260 BG

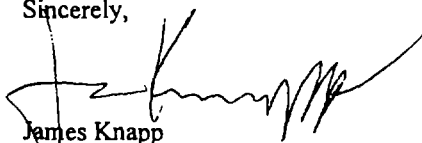
- A. As mentioned above, a table including the MDLs, PQLs, and RLs has been added to the back of the SOP. This table also includes *retention times*.
- B. A description of the mass spectrometer parameters has been added (Section 9.3). The laboratory does not currently perform SIM analyses.
- C. The concentration of the calibration standards has been included (Section 8.1.1).
- D. Refer to the MDL table mentioned above.
- E. Detects above the MDL but below the RL can be reported upon client request.
- F. Methyl iodide has been included in the primary characteristic ion table.

XI. PNAs by HPLC SOP GLA 8310 BG

- A. As mentioned above, a table including the MDLs, PQLs, and RLs has been added to the back of the SOP. Appendix A includes *retention times*.
- B. Fluorene has been added to the requested table.
- C. The concentration of the calibration standards has been added (Section 10.1.2).
- D. More discussion on the calibration procedures has been included (Sections 8.1 and 10.1.2).
- E. A description of the gradient program is included (Section 11.1).
- F. The equations for %Rec and RPD calculations have been added (Sections 11.5.1 and 11.5.2).

Please let me know if you have any questions or concerns. Have a great day!

Sincerely,


James Knapp
Quality Assurance Manager
Email : jknapp@glalabs.com

Enclosures

July 15, 1999

Margaret Karolyi
Carlson Environmental, Inc.
65 East Wacker Place
Suite 1500
Chicago, Illinois 60601

Dear Ms. Karolyi,

Enclosed is the response to the EPA's second round of comments on Great Lakes Analytical's standard operating procedures (SOPs) and performance data. The following outlines the actions taken to fulfill their requests:

GLA 1312 BG SOP—SPLP

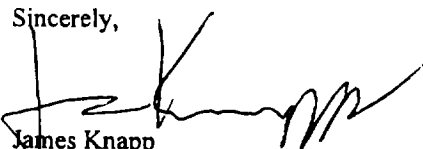
- A discussion on matrix spikes has been added to sections 6.2 and 11.2.8 of the SOP. However, specifics on spike concentrations will be found in the specific analytical method (ex. GLA 7000 BG for Pb).

GLA 160.1/4 BG SOP—Percent Organic Carbon

- The acceptance criteria for duplicate sample analysis has been added in section 6.4 of the SOP.
- Discussion of LCS and LCS duplicate preparation and analysis can be found in sections 6.3 and 11.4.2.
- An explanation on how to convert percentage to mg/Kg has been added to section 11.10.7.

Please let me know if you have any questions or concerns. Have a great day!

Sincerely,



James Knapp
Quality Assurance Manager
Email : jknapp@glalabs.com

Enclosures

July 19, 1999

Margaret Karolyi
Carlson Environmental, Inc.
65 East Wacker Place, Suite 1500
Chicaco, IL 60601

Dear Margaret,

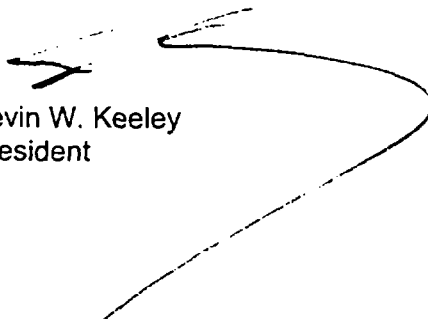
In response to our conversation today, I would like to clarify our plans regarding the analysis of samples for Tantalum from the Fansteel site.

Great Lakes Analytical has arranged for Sequoia Analytical in Walnut Creek California to analyze samples for rare metals not available from our Buffalo Grove laboratory. Sequoia Analytical, which shares common ownership with Great Lakes Analytical, has agreed to perform this analysis in accordance with the requirements specified in our Quality Assurance Plan.

As we discussed several months ago when we were forced to retire our sequential ICP, this is how we intend to handle the Tantalum analysis requirements at the Fansteel site. Upon receipt from the Fansteel site, samples will be logged in at Buffalo Grove. A sub-sample will then be sent to Sequoia Analytical-Walnut Creek for Tantalum analysis by sequential ICP. Great Lakes Analytical's Quality Assurance Plan will be followed. Analytical data will be transmitted to Great Lakes Analytical where it will be merged with our data and reported to Carlson Environmental. From our report it will be apparent that the Tantalum analysis was performed at Sequoia Analytical.

If you have any questions regarding our plans or Sequoia Analytical-Walnut Creek, please do not hesitate to contact me

Sincerely,



Kevin W. Keeley
President

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF TOTAL SOLIDS,

TOTAL DISSOLVED SOLIDS, TOTAL SUSPENDED SOLIDS,

TOTAL VOLATILE SOLIDS/PERCENT ASH, FRACTIONAL ORGANIC

CARBON, and ASTM TOTAL ORGANIC CARBON

GLA 160.1/4 BG

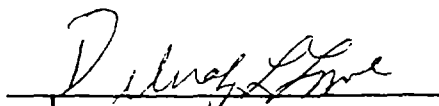

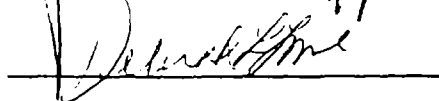
Revision 2.0

Approved By:

Department Manager:

Quality Assurance Manager:

Laboratory Director:

Date: 7/15/99

Date: 7/14/99

Date: 7/15/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of samples for total solids (residue), total dissolved (filterable) solids, total suspended solids, and/or total volatile solids. This SOP is an interpretation of the EPA Methods 160.1, 160.2, 160.3, and 160.4, Standard Methods no. 2540, sections B, C, D, and E, ASTM D2974-87, and Method SW-846 5035 Section 7.5. Instructions for the determination of free liquids in waste samples by the paint filter test are also included (Method SW846 9095A).

1.1 MATRICES

This procedure is applicable for the analysis of soils, solid waste, drinking, surface, and saline waters, and domestic and industrial wastes.

NOTE: Preservation of the sample is not practical or required, although analysis should begin as soon as possible. Refrigeration at 4°C to minimize microbiological decomposition of solids is recommended.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

2.1 Filterable (dissolved solids) residue (EPA 160.1, SM 2530-C): Filterable residue are those solids capable of passing through a glass fiber filter and being dried to constant weight at 180°C. A well-mixed aliquot of sample is filtered through a glass fiber filter. The filtrate is evaporated and the solids dried to constant weight at 180°C. The practical range of this determination is 10 to 20,000 mg/L. The solids retained on the filter may be dried at 103-105°C, and weighed for the determination of total suspended solids.

2.2 Non-filterable (suspended solids) residue (EPA 160.2, SM 2530-D): Non-filterable residue are those solids which are retained by a glass fiber filter and dried to constant weight at 103-105°C. A well-mixed sample is passed through a glass fiber filter, and the residue retained on the filter dried to constant weight at 103-105°C. The practical range of this determination is 4 to 20,000 mg/L.

2.3 Total residue (Total Solids or % Dry Weight; EPA 160.3, SM 2530-B, SW846 5035 Sec. 7.5): Total residue is the sum of the homogeneous suspended and dissolved materials in a sample. A well-mixed aliquot of sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105°C. The practical range of this determination is 10 to 20,000 mg/L.

NOTE: The results of the total filterable (dissolved) and total non-filterable (suspended) solids analyses CANNOT be mathematically added to obtain a total solids result.

11.11 Volatile residue (EPA 160.4, SM 2530-E): The dried residue obtained from the determination of total, filterable, or non-filterable residue is ignited at $550 \pm 50^\circ\text{C}$ in a muffle furnace for one hour or until all organic matter has ashed off. The remaining solids represent the fixed solids, while the weight lost on ignition is the volatile solids.

2.5 ASTM Fractional/Total Organic Carbon (ASTM D2974-87): Samples are prepared the same as for volatile residue, and ignited at $440 \pm 50^\circ\text{C}$ for a minimum of one hour or until all organic matter has ashed off and the sample is at a constant weight.

- 2.6 Paint filter liquids test (SW846 9095): A 100g sample is placed in a paint filter. If any liquid passes through and drops from the filter with 5 minutes, the material is considered to contain free liquids.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 COMPRESSED GASES

All compressed gases, except air, can cause suffocation by displacing oxygen. Caution should be exercised when changing compressed gas cylinders. Analysts must wear safety glasses when changing cylinders or working with gas plumbing. All compressed gas cylinders must be secured at all times. A handtruck must be used to transport cylinders. The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place.

3.4 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.5 HIGH TEMPERATURES AND MUFFLE FURNACE

- 3.5.1 High temperature gloves and tongs must be used when loading/unloading samples from the muffle furnace. Special care should be exercised in handling any sample which has not completely evaporated or combusted to prevent splashing of hot materials.
- 3.5.2 The muffle furnace is operated at a temperature of 400 - 600°C for the duration of this test. Contact with the heated surfaces of the furnace or sample crucibles can cause second and third degree burns as well as melt inappropriate materials onto the analyst's hands or arms if allowed to get too close. Appropriate high temperature gloves and long tongs are provided for loading and unloading the muffle furnace.
- 3.5.3 When analyzing anything but soils for total volatile solids, the muffle furnace must be relocated to in front of a fume hood. Fumes given off by the evaporation/combustion of samples during the ignition process can then be appropriately vented outside the lab.
- 3.5.4 Incomplete combustion of especially high organic bearing samples can saturate the air inside of the muffle furnace. If the door is opened under these conditions, a flash fire could occur due to the rapid oxidation of the organic laden atmosphere. The analyst must allow the

samples the minimum one hour of ignition time after loading the furnace to insure all organics have been combusted before opening the muffle furnace door.

4.0 INTERFERENCES

- 4.1 The principle source of error in these determinations is failure to obtain a representative sample. The analyst must be sure a representative portions of well-mixed samples are taken for analysis.
- 4.2 Highly mineralized waters and sludges containing significant amounts of calcium, magnesium, chloride or sulfate may be hygroscopic and will require prolonged drying, dessication, and rapid weighing. Non-representative solids, such as leaves, sticks, fish, etc., should be excluded from the sample if their inclusion is not representative of the material being sampled or desired in the final result. Too much residue in the drying dish may crust over and entrap water (total residue should be limited to about 200 mg).
- 4.3 Filterable (dissolved) solids - Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to ensure that all bicarbonate is converted to carbonate.
- 4.4 Non-filterable (suspended) solids - Samples high in filterable solids, such as saline waters, brines, and some industrial wastes, may exhibit a positive interference. Thoroughly wash the filter to ensure removal of dissolved materials.
- 4.5 Total solids/% Dry Weight - Floating oil and grease should be dispensed with a blender before analysis. Results from samples still containing non-volatile liquids, such as oils after the appropriate drying time must be flagged: "total solids partially due to liquids non-volatile at 103-105°C".
- 4.6 Total volatile solids - This test is subject to errors including: loss of water of crystallization, loss of organic matter prior to combustion, incomplete oxidation of organics, and decomposition of mineral salts. Therefore, the results cannot be considered an accurate measure of organic carbon in the sample.
- 4.7 Paint filter test - This test must be performed above the freezing point of any liquid in the sample.

5.0 RECORD KEEPING

- 5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.
- 5.2 Solids Log Book(s): A log book will be maintained for all determinations. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:
- | | |
|--|-----------------------------------|
| • Method reference number | • Sample matrix type |
| • Client Name for each set of samples | • Spiking volumes used |
| • GLA Sample I.D. (one complete for each set) | • Spike standard identifier |
| • Initial sample volume and weight used | • Spike standard concentration |
| • LIMS batch reference number | • LCS and LCS duplicate info |
| • Analyst's signature and date prepared/analyzed | • Final weights |
| • Data reviewer's signature and date | • Initial and final furnace temps |
| • All readings, dilution factors, and calculated results | |

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

- 5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a 5 % frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), and LCS duplicates. The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLES (LCS) AND LCS DUPLICATES

An external reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5 % frequency). For water matrices, the external standard is a solution of sodium chloride (See section 10.4). For soil samples, the external standard is clean sand. The results of the samples must have recoveries within established control limits, or where there is not enough data to calculate control limits, within 20 % of the known value. For solid matrices, the expected recovery is between 95 to 105%. The relative percent difference (%RPD) between the LCS and LCS duplicates must be within established control limits, or where there is not enough data to calculate control limits, within 20 % RPD.

6.4 DUPLICATE SAMPLES

For each batch of 20 or less, matrix-specific samples, a sample is analyzed in duplicate. The relative percent difference (%RPD) between the sample and its duplicate must be within established control limits, or where there is not enough data to calculate control limits, within 20 % RPD.

6.5 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.6 CORRECTIVE ACTION

A Corrective Action Report must be initiated any time the quality of the data could be questioned, or more specifically, when any of the following occur:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.

- A deviation from the normal SOP for the method is discovered (e.g. a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

- 7.1** The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory. Extraction Logbooks contain records of sample extractions and preparations for analytical batches.
- 7.2** Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "xxxx" and "xxxx?". The information includes:
- Client name.
 - Sample numbers.
 - Project name.
 - Matrix.
 - Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Control Manual.
- Copies of GLA SOP and source methods.
- Copies of the calibration studies and dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Surrogate standard recovery tabulations and control limits.
- Corrective action sheets.

8.2 INTERNAL AUDITS AND PERFORMANCE EVALUATION SAMPLES

Internal audits will be performed periodically to assess analytical system performance. These audits will be followed up to ensure that any deficiencies found have been eliminated and/or rectified. Performance evaluation samples will be periodically to assess laboratory performance (Refer to xxx)

9.0 EQUIPMENT

- 9.1** Glass evaporating dishes or porcelain crucibles, approx. 130 mL capacity.
- 9.2** Aluminum weighing dishes, numbered and categorized.
- 9.3** Porcelain Gooch crucibles.
- 9.4** Glass fiber filter disks, without binder, Gelman A/E or equivalent.
- 9.5** Suction flask, adapter and vacuum pump.
- 9.6** Drying oven, 103-105°C/180°C, with monitoring thermometer.
- 9.7** Analytical balance capable of weighing to 0.0001 g (0.1 mg).

- 9.8 Graduated cylinders, 25-250 mL size.
- 9.9 Dessicator.
- 9.10 Muffle furnace capable of attaining $550 \pm 50^{\circ}\text{C}$.
- 9.11 Polypropylene sample cups.

10.0 STANDARDS AND REAGENTS

- 10.1 Reagent water - ASTM Type II water (DI water).
- 10.2 Sodium Chloride - NaCl, crystal, Fisher no. xxx, or Mallinckrodt no. xxx.
- 10.3 Clean dry sand, purchased, Fisher no. xxx, or Mallinckrodt xxx.
- 10.4 Sodium chloride standard solution, 2000 mg/L NaCl - Accurately weigh approximately 2.0 g of NaCl and transfer to a 1000-mL volumetric flask. Dissolve, dilute to the mark with reagent water, and mix. Transfer to a 1-L plastic bottle. Keep tightly capped to minimize evaporation and subsequent concentration of the standard. Prepare solution annually or as needed.

11.0 PROCEDURES

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

- 11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis.***

11.2 PREPARATION OF EVAPORATING DISHES

- 11.2.1 For analysis of filterable and/or non-filterable solids, see section 11.3.
- 11.2.2 For analysis of total solids/% Dry Weight:
 - Aluminum weighing dishes for solids are cleaned and rinsed with reagent water, dried in the oven at $103-105^{\circ}\text{C}$ for a minimum of 1 hour, cooled and dessicated for a minimum of two hours before use.
 - Glass evaporating dishes used for waters are cleaned and rinsed with reagent water, dried in the muffle furnace at 350°C for a minimum of 1 hour, cooled and dessicated for a minimum of two hours before use.
 - Porcelain crucibles are used for non-aqueous liquids and non-aqueous liquid containing waters and sludges. They are cleaned and rinsed with reagent water, dried in the oven at $103-105^{\circ}\text{C}$ for a minimum of 1 hour, cooled and dessicated for a minimum of two hours before use.
- 11.2.3 For analysis of total volatile solids (only): Porcelain crucibles are used for analysis of total volatile solids. They are cleaned and rinsed with reagent water, then ignited in a muffle furnace at $550 \pm 50^{\circ}\text{C}$ for 1 hour, cooled and dessicated for a minimum of two hours before use.
- 11.2.4 For analysis of total volatile solids following analysis for dissolved or suspended solids: All porcelain Gooch and evaporating crucibles must be thoroughly cleaned with detergent and water, final rinsed with reagent water, then ignited in a muffle furnace at $550 \pm 50^{\circ}\text{C}$ for 1 hour, cooled and dessicated for a minimum of two hours before use.
- 11.2.5 Weigh each evaporating dish, crucible, or filter assembly, required for all QC and test samples, to the nearest 0.0001 g and record the crucible I.D.'s and weights in the appropriate log book.

11.3 PREPARATION OF FILTRATION ASSEMBLY

- 11.3.1 Gooch crucibles must be thoroughly cleaned before each use. If grease or oily coatings are not removed by normal cleaning with detergent and reagent water, or if the samples are also to be analyzed for total volatile solids, they should be ignited in a muffle furnace at $550 \pm 50^\circ\text{C}$ for 1 hour and cooled before use.
- 11.3.2 Place a glass fiber filter disk, wrinkled side up, in the Gooch crucible. Wet the disk with about 5 mL of reagent water to seat in the bottom of the crucible. Place crucible into the adapter and apply vacuum. Wash with three (3) successive volumes of reagent water and continue to apply vacuum until all traces of water have passed through.
- 11.3.3 If samples are to be analyzed for total filterable (dissolved) solids only, proceed to section 11.3.4. Else, dry crucible and filter together in the oven at $103\text{--}105^\circ\text{C}$ for a minimum of two hours. Remove to dessicator for one hour and weigh to the nearest 0.0001 g. Repeat cycle until a constant weight is obtained. Alternatively, prepare crucibles and filter and allow to dry in the oven at $103\text{--}105^\circ\text{C}$ overnight. Remove, and place in the dessicator for at least 1 hour before use.
- 11.3.4 Weigh each evaporating dish, crucible, or filter assembly, required for all QC and test samples, to the nearest 0.0001 g and record the crucible I.D.'s and weights in the appropriate log book.

11.4 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

- 11.4.1 For Method Blanks:
- Liquid samples
 - * For filterable (dissolved) and non-filterable (suspended) solids, 100 mL of reagent water is processed as a sample.
 - * For total solids and volatile solids, aliquot 50 mL of reagent water into a prepared, pre-weighed glass evaporating dish (if for analysis of volatile solids only, use a porcelain crucible). Record the weight of water and dish to the nearest 0.0001 g.
 - Solid samples
 - * For total solids and volatile solids, aliquot 10 mL of reagent water into a prepared, pre-weighed aluminum evaporating dish (if for analysis of volatile solids only, use a porcelain crucible). Record the weight of water and dish to the nearest 0.0001 g.
 - * Filterable and non-filterable solids are not determined for solid samples.
- 11.4.2 For Laboratory Control Samples (samples contain xx xx xx).
- Liquid samples
 - * For analysis of filterable solids (only), process two 100-mL aliquots of sodium chloride solution as samples.
 - * For non-filterable solids (only), weigh approximately 0.1 g of clean sand into a weigh boat. Record the actual weight. Quantitatively rinse the sand into a clean sample cup with approximately 100 mL of reagent water. Prepare two of these spikes for analysis and process as samples.
 - * For filterable and non-filterable solids, weigh approximately 0.1 g of clean sand into a weigh boat. Record the actual weight. Quantitatively rinse the sand into a clean sample cup with a 100-mL aliquot of sodium chloride solution. Prepare two of these spikes for analysis and process as samples.
 - * For total and volatile solids, aliquot 50 mL of sodium chloride solution into a prepared, pre-weighed glass evaporating dish (if for analysis of volatile solids only, place solution in a porcelain crucible). Record the volume of solution, and the weight of the solution and dish to the nearest 0.0001 g.

- Solid samples
 - * For ASTM Fractional/Total Organic Carbon, and total and volatile solids, weigh approximately 10 g of sand into a prepared, pre-weighed aluminum evaporating dish (if for analysis of volatile solids only, place sand in a porcelain crucible). Record the weight of the sand and dish to the nearest 0.0001 g. Add approximately 5 mL of reagent water.
 - * Filterable and non-filterable solids are not determined for solid samples.

11.4.3 For Test Samples:

There are no specific preparations of the samples other than thorough mixing immediately prior of analysis. Analyst observation is usually adequate for determining the proper amount of sample to use.

- Liquid samples
 - * For analysis of filterable (dissolved) and non-filterable (suspended) solids:
 - Filtration time should not exceed 10 minutes for samples containing high levels of suspended samples.
 - A larger sample must be used (250-500 mL) for samples with minimal amounts of suspended solids. The captured weight of solids must be at least 1.0 mg, or the data must be flagged as "insufficient sample to meet minimum method criteria."
 - * For total and volatile solids, place approximately 50 mL of sample into a prepared, pre-weighed glass evaporating dish (if for analysis of volatile solids only, place solution in a porcelain crucible). Record the volume of solution, and the weight of the solution and dish to the nearest 0.0001 g. For other aqueous liquids, aliquot 100 mL of samples with minimal amounts of solids apparent - use smaller volumes if solids are visible.
- Solid samples
 - * For total and volatile solids, place approximately 10 g of sample (including non-aqueous liquid samples) into a prepared, pre-weighed aluminum evaporating dish (if for analysis of volatile solids only, place sand in a pre-weighed porcelain crucible). Record the volume of solution, and the weight of the sand and dish to the nearest 0.0001 g.
 - * Filterable and non-filterable solids are not determined for solid samples.

11.4.4 Matrix spiked samples are not applicable nor required for these methods.

11.5 FILTRATION PROCEDURE FOR DISSOLVED AND SUSPENDED SOLIDS

11.5.1 Each sample/blank/spike is processed in turn by this procedure. Please note that some sections are not required depending upon the analyses being performed.

11.5.2 Inspect the crucible/filter assembly and insure that the filter is centered in the bottom of the crucible. Wet the filter with a small amount of reagent water to effect a good seal upon the application of vacuum.

11.5.3 ***For samples to be analyzed for total dissolved solids:*** Thoroughly clean the filtration flask, funnel and adapter with a final reagent water rinse before ***EVERY*** sample filtration.

9.8.2.2 Fit the crucible into the adapter of the filtration apparatus and switch on the vacuum pump.

11.5.3 Shake the sample container vigorously and ***IMMEDIATELY*** transfer a predetermined aliquot volume into the crucible using an appropriately sized, clean graduated cylinder. Remove all traces of water by allowing suction to remain on after the sample has passed through.

11.5.4 Rinse the sample with three successive washings of reagent water, approximately 10 mL per rinse. Be sure to rinse any droplets or particulates adhering to the sides of the crucible down into the filter as well, allowing for complete drainage between washings. Remove all traces of water by continuing to apply vacuum after water has passed through.

11.5.5 Switch off pump and allow vacuum to slowly release. Carefully remove the crucible from the adapter.

11.5.6 ***For samples to be analyzed for total dissolved solids:*** Quantitatively transfer the filtrates to appropriate evaporating dishes.

11.5.7 Proceed to section 11.6 for filterable solids, or 11.7 for non-filterable solids.

11.6 ANALYSIS FOR TOTAL FILTERABLE (DISSOLVED) SOLIDS

11.6.1 After transferring all samples to their respective evaporating dishes, dry the evaporating dishes in the oven at 103-105°C until all water is evaporated. This will probably take overnight.

11.6.2 Raise the oven temperature control to 180°C. When the temperature reaches and stabilizes at 180°C, record the initial oven temperature.

11.6.3 Dry the evaporating dishes in the oven at 180°C for a minimum of 1 hour. Samples exhibiting substantial amounts of dissolved solids should be allowed to dry for a longer period of time (even overnight) to evaporate potentially entrapped water and convert any bicarbonate to carbonate.

11.6.4 Record the final oven temperature. Remove dishes to the dessicator for at least 1 hour before weighing. Record final weight to the nearest 0.0001 g.

11.7 ANALYSIS FOR TOTAL NON-FILTERABLE (SUSPENDED) SOLIDS

11.7.1 Record the initial oven temperature.

11.7.2 Dry the gooch crucibles in the oven at 103-105°C for a minimum of 1 hour. Alternatively, allow the samples to dry in the oven at 103-105°C overnight.

11.7.3 Record the final oven temperature.

11.7.4 Remove the crucibles to dessicator for at least 1 hour, and weigh to the nearest 0.0001 g. If samples were dried overnight, record this as the final weight. If samples have been in the oven for the minimum 1 hour time period, repeat the drying/cooling/weighing cycle until a constant weight is obtained. Record this final weight.

11.8 ANALYSIS FOR TOTAL SOLIDS

11.8.1 Record initial temperature of oven.

11.8.2 Place all evaporating dishes in the oven at 103-105°C for a minimum of 4 hours for solid samples, or overnight (minimum of 8 hours) for waters and/or solids.

11.8.3 Record final temperature of oven.

11.8.4 After checking any waters for complete evaporation, remove samples from the oven and dessicate for at least one hour.

11.8.5 Weigh each sample/dish and record the final weight to the nearest 0.0001 g.

11.8.6 Analysis for **total solids** is complete at this step. Continue with section 11.9 for the analysis of **total volatile solids (TVS), % Ash, Organic Carbon Content (OCC), Fractional Organic Carbon (FOC), and ASTM Total Organic Carbon (TOC)**, if required.

11.9 ANALYSIS FOR TOTAL VOLATILE SOLIDS

NOTE: If any sample is suspected of having a high organic content that might produce large volumes of smoke or other fumes upon combustion, remove the muffle furnace to a laboratory cart and place in front of a fume hood in the inorganic lab area.

11.9.1 Adjust the muffle furnace temperature to $550 \pm 50^\circ\text{C}$ for TVS/%Ash, and to $440 \pm 50^\circ\text{C}$ for FOC, OCC, and ASTM TOC. Record the initial temperature of the muffle furnace.

11.9.2 While wearing high temperature gloves and using long tongs, load the QC and test samples into the muffle furnace. Due to space limitations in the muffle furnace, large numbers of samples will require that several "batches" be ignited separately. Be sure the muffle furnace door is closed completely and the latch is engaged.

11.11.4 Heat samples for one hour. **CAUTION: Do not open the muffle furnace door during this time.** The potentially vapor saturated could create a flash fire upon the inrush of air (oxygen).

11.9.4 After one hour, open the muffle furnace and observe the samples. If all the organic material has ashed off, go to section 11.9.5. If not, continue ignition for an additional one hour.

11.9.5 After one hour, record the final temperature of the muffle furnace.

11.9.6 Remove samples from the furnace and dessicate for at least one hour.

11.9.7 Weigh each sample/dish and record the final weight to the nearest 0.0001 g.

11.10 CALCULATIONS

11.10.1 Total filterable (dissolved) solids:

$$\text{Filterable solids, mg/L} = \frac{[\text{initial wt. (g)} - \text{final wt. (g)}] \times 1,000,000}{\text{volume of sample used (mL)}}$$

11.10.2 Total non-filterable (suspended) solids:

$$\text{Non-filterable solids, mg/L} = \frac{[\text{initial wt. (g)} - \text{final wt. (g)}] \times 1,000,000}{\text{volume sample used (mL)}}$$

11.10.3 Total solids as percent solids - % for solids/non-aqueous liquids:

$$\text{Percent total solids, \%} = \frac{[(C - A)] \times 100}{[(B - A)]}$$

where: A = initial tare weight of evaporating dish (g)
 B = weight of dish AND sample before drying (g)
 C = final weight of sample and dish after drying (g)

11.10.4 Total solids, as mg/kg, for solids - for solids/non-aqueous liquids:

$$\text{Total solids, mg/kg} = \frac{[(C - A)] \times 1,000,000}{[(B - A)]}$$

where: A = initial tare weight of evaporating dish (g)
 B = weight of dish AND sample before drying (g)
 C = final weight of sample and dish after drying (g)

11.10.5 Total solids, as mg/L, for waters:

$$\text{Total solids, mg/L} = \frac{[(C - A)] \times 1,000,000}{[(B)]}$$

where: A = initial tare weight of evaporating dish (g)
 B = volume of sample used (mL)
 C = final weight of sample and dish after drying (g)

11.10.6 Total volatile solids - % for solids or any liquids:

$$\text{Percent volatile solids, \%} = \frac{[(C - D)] \times 100}{[(C - A)]}$$

where: A = initial tare weight of crucible (g)
 C = final weight of sample and crucible after drying (g)
 D = final weight of sample and crucible after ignition (g)

11.10.7 Percent ash, FOC, OCC, ASTM TOC (fixed solids) - % for solids or any liquids:

$$\text{Percent ash, Percent Organic Carbon, \%} = \frac{[(D - A)] \times 100}{[(C - A)]}$$

where: A = initial tare weight of crucible (g)
 C = final weight of sample and crucible after drying (g)
 D = final weight of sample and crucible after ignition (g)

To convert % Ash and % Organic Carbon to mg/Kg, multiple the percentage by 10000.

11.10.8 Total volatile solids (mg/L) for waters:

$$\text{Total volatile solids, mg/L} = \frac{[(C - D)] \times 1,000,000}{[(B)]}$$

where: B = volume of sample used (mL)
 C = final weight of sample and crucible after drying (g)
 D = final weight of sample and crucible after ignition (g)

11.10.9 Total fixed solids (mg/L) for waters:

$$\text{Total volatile solids, mg/L} = \frac{[(D - A)] \times 1,000,000}{[(B)]}$$

where: A = initial tare weight of evaporating dish (g)
 B = volume of sample used (mL)
 D = final weight of sample and crucible after ignition (g)

11.10.10 Calculation notes:

Any sample with liquid(s) (e.g. - oils or grease) which are not volatile at 103-105°C must be flagged "total solids partially due to liquids non-volatile at 103-105°C".

11.10.11 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.10.12 Relative Percent Difference (%RPD) for duplicate analyses:

$$\% \text{ RPD} = \frac{|\text{Conc. of 1}^{\text{st}} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of 1}^{\text{st}} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

11.11 PAINT FILTER TEST

11.11.4 Assemble test apparatus as shown in Figure 1.

11.11.2 Place sample in filter. Settling the sample into the filter may be facilitated by lightly tapping the side of the filter/funnel.

NOTE: In order to assure uniformity and standardization of the test, materials which do not conform to the shape of the filter (such as sorbent pads or pillows) should be cut into small pieces using scissors, shears, or a knife. The integrity of the sorbent fabric should be preserved as much as possible. The particles to be tested should be reduced to about 9-mm in size. Grinding sorbent materials should be avoided as this may destroy the integrity of the sorbent and produce may "fine particles" which would not be normally present. Light crushing is acceptable for brittle materials larger than 1 cm that do not conform to the filter (such as clay, silica gel, and some polymers, which are not practical to cut).

11.11.3 Allow sample to drain for 5 minutes into the graduated cylinder.

11.11.4 If any portion of the test material collects in the graduated cylinder during the 5-minute period, the material is deemed to contain free liquids.

11.11.5 Any sample containing free liquids is reported as a "Fail". Samples that do not contain free liquids are reported as "Pass".

12.0 MAINTENANCE AND TROUBLESHOOTING**12.1 GENERAL**

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

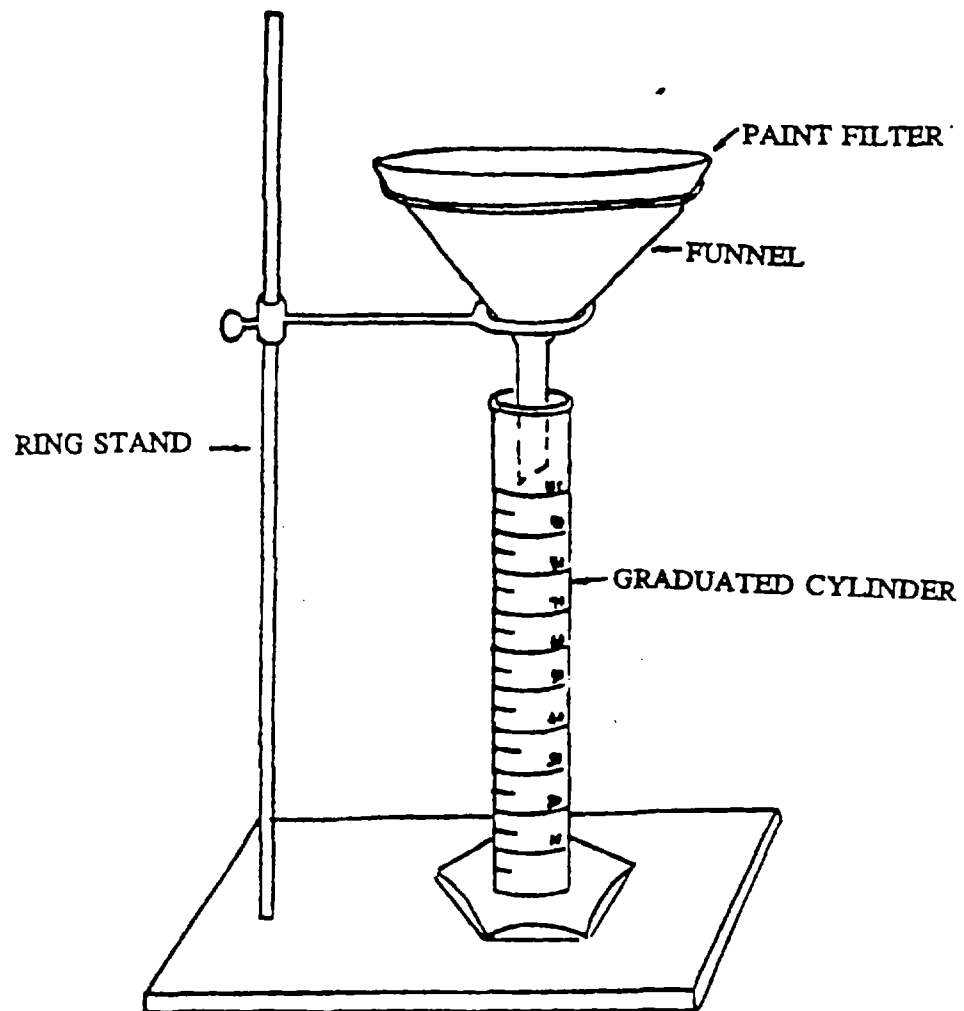
Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be used who may be unsure of the instrumentation and a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

13.0 REFERENCES

- 13.1 EPA Method 160.1: Residue, Filterable (Gravimetric, dried at 180°C).
- 13.2 EPA Method 160.2: Residue, Non-filterable (Gravimetric, dried at 103-105°C).
- 13.3 EPA Method 160.3: Residue, Total (Gravimetric, dried at 103-105°C).
- 13.4 EPA Method 160.4: Residue, Volatile (Gravimetric, ignition at 550°C).
- 13.5 Standard Methods no. 2540: Solids - section B, Total Solids Dried at 103-105°C.
- 13.6 Standard Methods no. 2540: Solids - section C, Total Dissolved Solids Dried at 180°C.
- 13.7 Standard Methods no. 2540: Solids - section D, Total Suspended Solids Dried at 103-105°C.
- 13.8 Standard Methods no. 2540: Solids - section E, Fixed and Volatile Solids Ignited at 500°C.
- 13.9 SW-846 Method 5035, Section 7.5, Dry Weight.
- 13.10 SW-846 Method 9095, Paint Filter
- 13.11 ASTM Method D2974-87, Total Organic Carbon
- 13.12 Great Lakes Analytical Quality Assurance Program Manual.
- 13.13 Great Lakes Analytical Chemical Hygiene Plan.
- 13.14 Great Lakes Analytical SOP for Login Department.
- 13.15 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to the Great Lakes Analytical Quality Assurance Program Manual.

Figure 1.**Paint Filter Test Apparatus.**

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF MERCURY IN


LIQUIDS AND SOLIDS

GLA 245.1/5 BG

Revision 2.0

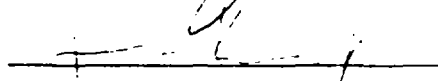
Approved By

Department Manager



Date 2/16/98

Quality Assurance Manager



Date 2/16/98

Laboratory Director



Date 2/16/98

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the determination of mercury by cold-vapor atomic absorption spectrophotometry. This SOP is an interpretation of EPA Methods 245.1 and 245.5, Standard Methods no. 3112, Section B, and methods SW-846 no's 7470A and 7471A. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for aqueous, solid, and mixed samples including soils, sediments, sludge, domestic and industrial wastes. Concentration range for samples is typically 0.2 to 2.5 ppb. Higher concentrations may be determined by sample dilution.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

Liquid samples are digested with nitric and sulfuric acids, potassium permanganate and potassium persulfate. Solid samples are digested with *aqua regia* (nitric and hydrochloric acids) and potassium permanganate. A series of standards is digested and analyzed concurrently to produce a calibration curve from which sample results are determined.

A semi-automatic cold-vapor apparatus is used to produce metallic mercury vapor from the resultant digestates. The sample is automatically mixed with hydrochloric acid and stannous chloride solution. The mercury is reduced to the elemental state which is then bubbled out of solution and carried into the instrumental light path by means of an inert argon gas flow. The atomic absorption of this vapor is read at 253.7 nm. Deuterium arc background correction is used to automatically correct for interference due to water vapor, chlorine, or other contaminants which absorb or block light at this wavelength. The absorption read by the spectrophotometer is proportional to the concentration of mercury in the original sample.

See Appendix A for method exceptions.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical (GLA) Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The GLA Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 METHOD SPECIFIC CHEMICALS

Potassium permanganate and persulfate are strong oxidizers. They can burn eyes and skin. Also, they can cause a fire if mixed with incompatible chemicals.

4.0 INTERFERENCES

- 4.1 Potassium permanganate is added to eliminate any possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide (as sodium sulfide) do not interfere.
- 4.2 Concentrations of copper as high as 10 mg/L do not interfere. Higher concentrations may cause interference.
- 4.3 Samples containing high levels of chlorides (such as sea water, brine, and industrial effluents) may require additional permanganate. Chlorides are converted to free chlorine, which also absorbs at 253 nm. Chlorine is eliminated before the reduction of mercury by using an excess of hydroxylamine reagent.
- 4.4 Certain volatile organic materials that absorb in the 253 nm region may also cause interference. A preliminary run without reagents should determine if this type of interference is present in samples. Deuterium arc background correction is used to automatically correct for these interferences.
- 4.5 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with DI water. Periodic cleaning of sample preparation and analysis areas will be performed.

5.0 RECORD KEEPING

- 5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.

- 5.2 Mercury Log Book

A log book will be maintained for all mercury determinations. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- GLA Sample I.D. (one complete for each set)
- Initial sample volume or weight used
- Final volume of digestates
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Time/temperature of water bath (initial and every 30 minutes)
- Calibration standard identifiers and concentrations
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Reviewer's signature and date

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

- 5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample ID numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5 % frequency (i.e. one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (e.g. PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (i.e. minimum 5 % frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15 % of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5 % (e.g. one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25 % of the known value.

6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (e.g. wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (e.g. a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedures for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 **Sample Schedule:** Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for mercury analysis are queued under "xxxx"=FLAA. The information includes:

- Client name.
- Sample numbers
- Project name
- Matrix.
- Hold time and turnaround time

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods
- Copies of the calibration studies and dates in use.
- Copy of the precision and accuracy study for the method
- Copies of all method detection limit studies and dates in use
- Check standard recovery tabulations and control limits
- Spike and spike duplicate recovery tabulations and control limits
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

8.3 METHOD DETECTION LIMIT STUDY

8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.

- Calculate the MDL by taking the standard deviation of the results of the 7 replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for 7 replicates)
- 8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.
- 8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

- 9.1 Atomic absorption spectrophotometer - fitted with a mercury hollow cathode lamp, capable of allowing the absorption cell to be mounted in a stable fashion in the light path of the instrument, Varian 600 DBQ, and able to correct for non-atomic absorption at the selected analytical wavelength, or equivalent.
- 9.2 Absorption cell - 10 cm long with UV-transparent quartz windows.
- 9.3 Cold mercury vapor generator - for proper proportional mixing of mercury reducing agents and physical vapor generation, Varian VGA 77, or equivalent.
- 9.4 300-mL capacity BOD bottle with stoppers
- 9.5 Hot plate/water bath - capable of maintaining 95°C
- 9.6 Thermometer - to accurately monitor the water bath for range 95-100°C
- 9.7 Graduated cylinders, 100-mL size
- 9.8 Pipettors and tips, 5-10 mL size.
- 9.9 Analytical balance capable of weighing to nearest 0.1 g
- 9.10 5-20 mL dispensers with bottle.

10.0 STANDARDS AND REAGENTS

- 10.1 Reagent water - ASTM Type II or equivalent (DI water).
- 10.2 Sulfuric acid - concentrated H_2SO_4 , Fisher no. A300 **CAUTION:** Sulfuric acid is corrosive.
- 10.3 Nitric acid - concentrated HNO_3 , Fisher no. A509 **CAUTION:** Nitric acid is corrosive.
- 10.4 Hydrochloric acid - concentrated HCl , Fisher no. A503 **CAUTION:** Hydrochloric acid is corrosive.
- 10.5 Aqua regia, 50% - Prepare immediately before use. First make aqua regia by carefully adding 3 volumes of concentrated HCl to 1 volume of concentrated HNO_3 . Then mix equal volumes of the aqua regia with reagent water. **CAUTION:** Aqua regia gives off extremely corrosive, irritating fumes. All handling of aqua regia should be performed in a fume hood.
- 10.5 Hydrochloric acid, 5 N - Dilute 40 mL of concentrated HCl to 100 mL with reagent water.
- 10.6 Hydrochloric acid, 20% v/v - Dilute 20 mL of concentrated HCl to 100 mL with reagent water.
- 10.7 Potassium permanganate - KMnO_4 crystals, Fisher no. P279 or Mallinckrodt no. 7068 **CAUTION:** Oxidizer.
- 10.8 Potassium permanganate solution - Dissolve 5 g of KMnO_4 per 100 mL of reagent water.
- 10.9 Potassium persulfate - $\text{K}_2\text{S}_2\text{O}_8$ crystal, Merck no. PX1560-1 or Mallinckrodt no. 7076 **CAUTION:** Oxidizer.
- 10.10 Potassium persulfate solution - Dissolve 5 g of $\text{K}_2\text{S}_2\text{O}_8$ per 100 mL of reagent water.
- 10.11 Hydroxylamine hydrochloride - $\text{NH}_2\text{OH}\cdot\text{HCl}$ crystals, Fisher no. H330 or Mallinckrodt no. 7581.
- 10.12 Sodium chloride - NaCl crystals, Fisher no. S271 or Mallinckrodt no. 7581.
- 10.13 Hydroxylamine hydrochloride solution - Dissolve 12 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 12 g of NaCl per 100 mL of reagent water.
- 10.14 Stannous chloride dihydrate - Tin (II) chloride dihydrate, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ crystals, Fisher no. T142, or Mallinckrodt no. 8176.
- 10.15 Stannous chloride solution - Add 25 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ per 100 mL of 20% v/v hydrochloric acid. Mix well to dissolve. Prepare fresh weekly. Discard if precipitation occurs.

- 10.16 Mercury stock standard solutions, 1000 ppb - use 2 different suppliers for solutions "A" and "B". Ultra Scientific no. ICP-080, Fisher no. SM114, Mallinckrodt no. H548
- 10.17 Mercury working standard solutions, 1 ppm (1000 ppb) - "A" Add 0.15 mL of concentrated HNO_3 to a 100-mL volumetric flask and add 50 mL of reagent water. Aliquot 0.10 mL of mercury stock standard solution "A" into the flask, dilute to the mark, and mix. Repeat for mercury spiking standard "B", except using mercury stock standard solution "B". Prepare fresh monthly.

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

- 11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the appropriate log book(s) *before beginning analysis*.

- 11.2.1 Method Validation Study - A method validation study must be performed, including a method detection limit determination. (Refer to section 10.7 for details.)

11.2 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

- 11.2.1 For Method Blanks:

- Liquid samples - Aliquot 100 mL of reagent water into a BOD bottle.
- Solid samples - Place 0.5 g of clean sand into a BOD bottle.
- Wipe samples - Place a 15cm Whatman 41 filter paper into a BOD bottle.

- 11.2.2 For Laboratory Control Samples (samples contain 1.0 ppb Hg):

- Liquid samples - Aliquot 100 mL of reagent water into a BOD bottle. Accurately aliquot 0.10 mL of mercury spiking standard "B" into the bottle.
- Solid samples - Place 0.5 g of clean sand into a BOD bottle. Accurately aliquot 0.10 mL of mercury spiking standard "B" into the bottle.
- Wipe samples - Place a 15cm Whatman 41 filter paper into a BOD bottle. Accurately aliquot 0.10 mL of mercury spiking standard "B" into the bottle.

- 11.2.3 For Test Samples:

- Aqueous liquids - Aliquot a 100-mL portion of well-mixed sample in a BOD bottle.
- Non-aqueous liquids - Transfer a **representative** 10-50 mL aliquot of well-mixed sample into a BOD bottle. Add reagent water to the bottle to bring the total volume to 100 mL.
- Mixed liquids (aqueous/non-aqueous) - The sample should be well-mixed before pouring a representative aliquot. The analyst should use his/her own judgement in determining the proper aliquot size so as not to exceed 20% non-aqueous liquid in the sample. If less than 100 mL is used, add reagent water to bring the total volume to 100 mL.
- Solid samples - A representative 0.5 g portion of sample is weighed and placed in a BOD bottle (for samples with a high water content, be sure the sample is mixed thoroughly). For samples of mixed solid types, particle size reduction and mixing may be required to ensure that a representative sample is analyzed.
- Wipes samples - The entire wipe is placed into the BOD bottle and the sample container rinsed into the BOD bottle with about 5mL of water.

- 11.2.4 For Matrix Spike Samples (samples have 1.0 ppb Hg added):

- Liquid samples - Aliquot two additional 100-mL portions of one sample, making sure to sample as homogeneous a mixture as possible. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each replicate. Mark as MS and MSD.
- Non-aqueous liquids - Transfer two additional representative 10-50 mL aliquots of well-mixed sample into BOD bottles. Add reagent water to the bottles to bring the total

volume to 100 mL. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each bottle, and label as MS and MSD.

- **Mixed liquids (aqueous/non-aqueous)** - The sample should be well-mixed before pouring a representative aliquot. Do not exceed 20% non-aqueous liquid in the sample. If less than 100 mL is used, add reagent water to bring the total volume to 100 mL. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each bottle, and mark as MS and MSD.
- **Solid samples** - Two additional representative 0.5 g portions of one sample are weighed and placed into BOD bottles. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each bottle and label as MS and MSD.
- **Wipes samples** - Two additional wipes are placed into two BOD bottles (1 each), and the sample containers rinsed with a minimum amount of reagent water. Accurately aliquot 0.10 mL of spiking standard "B" into each bottle. Mark as MS and MSD.

11.3 PREPARATION OF CALIBRATION AND CHECK STANDARDS

11.3.1 Add 100 mL of reagent water to each of 6 BOD bottles. Aliquot 0.00, 0.05, 0.10, 0.15, 0.20, and 0.25 mL of mercury working standard "A" into the bottles to produce a set of calibration standards of 0.00, 0.50, 1.00, 1.50, 2.00, and 2.50 ppb mercury.

11.3.2 Add 100 mL of reagent water and 0.10 mL of mercury spiking standard "B" to a BOD bottle, producing a 1.0 ppb check standard.

11.4 DIGESTION OF LIQUIDS

See section 11.5 for digestion of solids.

CAUTION: The heated reaction in the BOD bottles produces gases and steam which will cause significant pressure. Bottle stoppers should be wet with water prior to placing in the bottle necks to prevent freezing up and allowing the samples to outgas.

11.4.1 Carry all standards and samples through all steps of the digestion procedure.

11.4.2 Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 , mixing after each addition.

11.4.3 Add 15 mL of potassium permanganate solution. Allow samples to stand for 15 minutes. If the purple color fades, add additional permanganate, noting in the log book how much additional permanganate has been added. Once the purple color has persisted for 15 minutes, proceed to the next step.

11.4.4 Add 3 mL of potassium persulfate solution, and place in the water bath for 2 hours at 95-100°C. Monitor and record the temperature of the water bath initially and every 30 minutes, adding boiling water to the bath as necessary to keep the bath level above the level of sample in the BOD bottles.

11.4.5 After the heating period, remove the sample bottles, cool, and add 6 mL of hydroxylamine hydrochloride solution (reduces excess permanganate).

11.5 DIGESTION OF SOLIDS

See section 11.4 for digestion of liquids.

CAUTION: The heated reaction in the BOD bottles produces gases and steam which will cause significant pressure. Bottle stoppers should be wet with water prior to placing in the bottle necks to prevent freezing up and allowing the samples to outgas.

- 11.5.1 Carry all standards and samples through all steps of the digestion procedure.
- 11.5.2 For solids: Add 10 mL of 50% *aqua regia*. Heat in a water bath at 95°C for 2 minutes.
- 11.5.3 Cool, and add 50 mL of reagent water and 15 mL of potassium permanganate solution.
- 11.5.4 Place in the water bath for 30 minutes at 95-100°C.
- 11.5.5 After the heating period, remove the sample bottles, cool, and add 6 mL of hydroxylamine hydrochloride solution (reduces excess permanganate). Add 50 mL of reagent water and mix.

11.6 ANALYTICAL PROCEDURE

- 11.6.1 Refer to the manufacturer's instruction manual for instrument set-up and operation. See Appendix B for a condensed list of operating instructions.
- 11.6.2 Calibration - The analyst will be prompted for the calibration blank and each standard in turn. The digests will be processed and analyzed by the instrument and the resultant absorbencies used to construct a calibration curve. The curve must have a correlation coefficient of 0.995 or greater to be valid. If not, the instrument will attempt a second calibration. If this fails, the operator must stop the run and determine the problem and correct before continuing.
- 11.6.3 A typical batch is analyzed according to the following protocol:
- 1) Calibration blank - result must be < detection level (0.0002 ppb).
 - 2) Initial check standard - result must be within $\pm 10\%$.
 - 3) Repeat check standard (optional) - same as check standard.
 - 4) High calibration standard - result must be within $\pm 10\%$ or within established control limits.
 - 5) Method blank - result must be < detection level (0.0002 ppb).
 - 6) LCS samples - result must be within $\pm 15\%$ or within established control limits.
 - 7) Unspiked matrix test sample.
 - 8-9) Matrix spikes - result must be within $\pm 25\%$ or within established control limits.
 - 10+) Balance of test samples. Include a check standard every 10 samples (or less) - the check standard must be $\pm 20\%$, or the run paused, problem corrected, and any samples run since the last passing check standard re-analyzed.

NOTE: Samples with a high level of suspended solids may require settling or filtration prior to analysis to prevent blockage of the pump tubing.

- 11.6.4 If a sample analysis is significantly high out of range, and "poisoning" of the system is suspected, a reagent blank should be analyzed repeatedly until it produces results below the reporting limit. If this isn't accomplished, the system is cleaned, recalibrated, and the affected samples reanalyzed.

11.7 CALCULATIONS

After a run has been completed and all of the verification standards are in control, the data may be calculated and reported:

For liquids:

$$\text{mg/L Hg} = \frac{\text{analyzed concentration} \times \text{dilution factor} \times 100}{1000 \times \text{volume used (mL)}}$$

$$\text{detection limit (DL) (mg/L)} = \frac{0.2 \times 100}{1000 \times \text{volume used (mL)}}$$

For solids:

$$\text{mg/kg Hg} = \frac{\text{analyzed concentration} \times \text{dilution factor} \times 100}{\text{weight used (g)}} \div 1000$$

$$\text{detection limit (DL, mg/L)} = \frac{0.2 \times 100}{\text{weight used (g)}} \div 1000$$

The dilution factor is 1, **unless** additional dilution of the sample was done
 '1000' is the conversion factor for ppb to ppm (mg/L)

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. See Appendix C for glassware cleaning instructions. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

13.0 REFERENCES

- 13.1 EPA Methods 245.1: Mercury (Manual Cold Vapor Technique), and 245.5: Mercury in Sediment (Manual Cold Vapor Technique).
- 13.2 Method 3112: Metals by Cold-Vapor Atomic Absorption Spectrometry, Section B: Mercury, Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
- 13.3 Methods SW-846 - 7470A: Mercury in Liquid Waste (Manual cold-vapor technique); and 7471A: Mercury in Solid or Semisolid Waste (Manual cold-vapor technique)
- 13.3 Great Lakes Analytical Quality Assurance Program Manual
- 13.4 Great Lakes Analytical Chemical Hygiene Plan
- 13.5 Great Lakes Analytical SOP for Login Department
- 13.6 Great Lakes Analytical SOP for Hazardous Sample Management

14.0 DEFINITIONS

See References

APPENDIX A.**METHOD EXCEPTIONS.**

- A.1 A semi-automated continuous-flow mercury vapor (hydride generator) is used to produce the cold mercury vapor. The automatic nature of the peristaltic pump and mixing manifold provides much enhanced stability and consistency in absorbance readings.
- A.2 A calibration range more appropriate to the detection levels required and concentrations of routine samples has been selected at 0.0 to 2.5 ppb.
- A.3 For solids, a single 0.5 g portion of sample is used for the analysis. Past performance of P.E. samples and replicate data has shown this procedure to produce accurate and precise results.
- A.4 The dead air space in the BOD bottle does not need to be purged before processing the sample through the cold-vapor generator because the final reaction does not occur in the BOD bottle.

APPENDIX B.**CONDENSED FLAA OPERATING INSTRUCTIONS**

- B.1 Sequence:
- Modify an existing sequence
 - OK
- B.2 Select sequence:
- Mercury 05/27/97, Hex Chrome
 - OK
 - 4 Hg Vapor, 99 Cr Flame Hexachrome
 - Error protocol
 - Next
 - Exit and switch to instrument window
 - OK
- B.3 Optimize:
- Rescale
 - Instrument zero
- B.4 Return:
- Start autorun
 - Meta - Matrix - Date
 - Analyst's initials
 - OK
 - Prompt Present Rinse
 - OK
 - Calibrate 0.0 0.5 1.0 1.5 2.0 2.5 ppm

APPENDIX C.**METALS GLASSWARE PREPARATION**

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.
2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.
3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware uniquely etched, cracked or otherwise likely break and/or cause contamination of samples.
4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test (e.g., dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF TOTAL CYANIDE, REACTIVE

CYANIDE, AND CYANIDE AMENABLE TO CHLORINATION

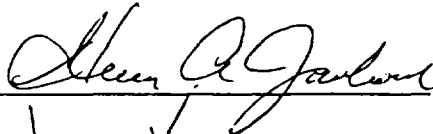
IN LIQUIDS AND SOLIDS

GLA 335.4 BG

Revision 2.1

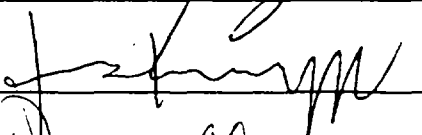
Approved By:

Department Manager:



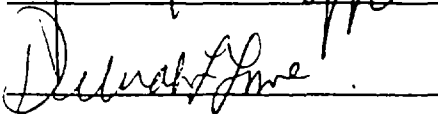
Date: 5/27/99

Quality Assurance Manager:



Date: 5/27/99

Laboratory Director:



Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the handling, digestion, and distillation of liquid and solid samples for the analysis of total cyanide, reactive cyanide (weak-acid dissociable cyanide), and cyanide amenable to chlorination. This SOP is an interpretation of EPA Method 335.4, Standard Methods no. 4500-CN⁻, and SW-846 Methods 9010B and 9012A.

1.1 MATRICES

This SOP may be used for drinking, ground, surface and saline waters, domestic and industrial waste, (solid, and mixed samples). Concentration range for samples is typically 5 to 1000 µg/L. Higher concentrations may be determined by sample dilution. Samples are preserved by addition of 2 mL of 10 N sodium hydroxide per liter and refrigeration.

NOTE: Distillates and solutions produced for this SOP are only applicable for the analysis method specified and are unacceptable for any other anionic or cationic analyses.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

Sulfuric acid is added to samples. Cyanide is released from the sample as volatile hydrocyanic acid (hydrogen cyanide, or HCN) and absorbed in a gas scrubber containing sodium hydroxide. Cyanide is then converted to cyanogen chloride (CNCl) by reaction with chloramine-T. CNCl forms a red-blue dye color upon the addition of a pyridine-barbituric acid reagent. The absorbance of this dye is measured at 580 nm.

For the analysis of total cyanide, the sample is treated for interferences and then refluxed with sulfuric acid. For the determination of cyanides amenable to chlorination, duplicate samples are portioned out. One sample is treated with excess chlorine (as calcium hypochlorite) for one hour. The excess hypochlorite is destroyed with sodium arsenite and total cyanide determined for both treated and untreated samples. The amenable cyanide is the total cyanide less the residual cyanide determined on the chlorinated sample.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 METHOD SPECIFIC CHEMICALS

Cyanide is acutely toxic, and in the presence of acid produces highly toxic and volatile HCN (hydrocyanic acid) fumes. All handling of cyanide solutions and salts will be performed with proper gloves and ventilation. All fumes produced by the distillation procedure will be evacuated to an appropriate hood or ventilation source. When performing the amenable cyanide preparation, cyanides react with chlorine to produce CNCl (cyanogen chloride) which is extremely toxic. All amenable cyanide preparations will be performed in a fume hood.

Pyridine is a toxic organic which has a permeating, irritating odor. It is readily absorbed through the respiratory tract and skin. Operations involving large amounts of pyridine will be carried out in a fume hood and proper gloves should be worn. Waste from the analytical process containing pyridine should be covered with parafilm to minimize volatilization of the material.

4.0 INTERFERENCES

- 4.1 Several different interferences are encountered with this method. Most are removed by the distillation process. Those interferences requiring pre-treatment or special treatment of the sample are addressed below.
- 4.2 Sulfides produce hydrogen sulfide during the distillation which adversely affects colorimetric, titrimetric, and electrode procedures. Samples are tested for sulfides with lead acetate paper. Bismuth nitrate solution is added to samples testing positive for sulfides to remove the interference.
- 4.3 Oxidizing agents such as chlorine decompose most cyanides. Samples are tested for oxidizers with KI-starch paper. Samples exhibiting positive results for oxidizers are treated with ascorbic acid until a negative test for oxidizers is obtained.
- 4.4 Nitrate and nitrite may produce a high bias to results. These ions produce nitrous acid which in turn can react with certain organic compounds to produce oximes. These oximes decompose to generate HCN. Interference from nitrates and nitrites is removed by the addition of sulfamic acid to the sample.
- 4.5 Carbonate in high concentrations may affect the distillation procedure by causing the violent release of carbon dioxide with excessive foaming when acid is added before distillation. Calcium hydroxide may be used to preserve such samples.

5.0 RECORD KEEPING

- 5.1 The analyst is responsible for keeping accurate and up-to-date records of all distillations and analyses performed.
- 5.2 Total Cyanide Log Book

A log book will be maintained for all cyanide distillations and determinations. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample volume or weight used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Data reviewer's signature and date
- Calibration standard identifiers and concentrations
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final distillate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out. Examples of a log book cover page and reagent preparation sheets are provided in Appendix A of this SOP.

- 5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 10% frequency (*i.e.* one set with every batch of ten or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of ten or less samples (*i.e.* minimum 10 % frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% (10% for drinking waters) of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 10% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 METHOD OF STANDARD ADDITIONS

The method of standard additions is used for the analysis of all samples that have matrix interferences such as sulfides. This procedure involves adding equal volumes of sample to a reagent water blank and to a standard. The higher the degree of accuracy needed, the greater the number of standard additions. The analytical signal for each of the prepared solutions is plotted on the vertical axis, with the corresponding standard concentrations plotted on the horizontal axis. When the resulting line is extrapolated back to zero analytical signal, the point at which the line crosses the horizontal axis is the concentration (absolute value) of the sample. The results are considered valid if:

- the plotted curve is linear over the concentration range of concern (slope should be less than 20% different than the slope of the calibration curve).
- the effect of the interference does not vary as the ratio of analyte concentration to sample matrix changes and the standard addition responds in a similar manner as the analyte.
- the determination is free of spectral interferences and corrected for nonspecific background interference.

For a single-addition method, the concentration would be calculated as follows:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_x}$$

where: C_x = Concentration of the sample

S_B = The analytical signal for the sample and water solution (corrected for the blank)

V_S = Volume of the standard solution added

C_S = Concentration of the standard solution added

S_A = The analytical signal for the sample and standard solution (corrected for the blank)

V_x = Volume of the sample added to each solution.

Note: V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_x , and thus C_S is much greater than C_x , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

6.8 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken to document steps taken to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (e.g. a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

- 7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.
- 7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "AUTO". The information includes:
- Client name.
 - Sample numbers.
 - Project name.
 - Matrix.
 - Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Control Manual.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 INTERNAL AUDITS AND PERFORMANCE EVALUATION SAMPLES

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Plan.)

8.3 METHOD DETECTION LIMIT STUDY

- 8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:
- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
 - Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).
- 8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

- 8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

- 9.1 Glassware required for each distillation set-up:
- 500-mL round bottom boiling flask.
 - Two-neck Claisen adapter with 24/40 ground glass joints.
 - Allihn condenser with 24/40 ground glass joints.
 - Tubing adapter with PTFE stopcock.
 - 125-250 mL gas scrubbing bottle.
 - Gas scrubber/stopper with fritted end.
 - 300-mm thimble top tube funnels.
 - 100-250 mL volumetric flasks.
 - 100-250 mL graduated cylinders.
- 9.2 Heating mantle(s) for 500-mL round bottom flasks with adjustable temperature control.
- 9.3 Tygon tubing for connecting glass apparatus.
- 9.4 Analytical balance capable of weighing to the nearest 0.1 grams.
- 9.5 Lachat Quikchem AE Auto analyzer - capable of delivering and reacting samples and reagents for automated continuous flow analysis, including:
- Sampling device.
 - Multi-channel pump.
 - Reaction/mixing manifold for cyanide.
 - Colorimetric detector.
 - Data acquisition device (computer).
- 9.6 Lead acetate paper, Fisher no. 14-862.
- 9.7 Potassium iodide (KI)-starch paper, Fisher no. 14-860.
- 9.8 Teflon-coated stir bars and magnetic stir plate.

10.0 STANDARDS AND REAGENTS

- 10.1 Reagent water - ASTM Type II or equivalent (DI water).
- 10.2 Ascorbic acid - crystal, ACS, analytical reagent grade, or USP, Mallinckrodt no. 1852.
- 10.3 Bismuth nitrate pentahydrate - $\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$, Fisher no. B337, or Mallinckrodt no. 0256.
- 10.4 Bismuth nitrate, 0.062 M - Dissolve 30.0 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$ into 100 mL of reagent water in a 1-L reagent bottle. Add 250 mL of glacial acetic acid while stirring. Dilute to 1 L with reagent water and mix.
- 10.5 Calcium hypochlorite - $\text{Ca}(\text{OCl})_2$, Fisher no. C100.
- 10.6 Calcium hypochlorite, ~5% - Dissolve 50 g of $\text{Ca}(\text{OCl})_2$ in 1000 mL of reagent water. Store protected from light exposure for up to one month.
- 10.7 Sodium hydroxide - NaOH pellets, Fisher no. S318, or Mallinckrodt no. 7708. **CAUTION:** Sodium hydroxide is corrosive.
- 10.8 Sodium hydroxide solution, 1.25 N - Dissolve 50 g of NaOH per liter of reagent water.
- 10.9 Sulfamic acid - $\text{H}_2\text{NSO}_3\text{H}$, Fisher no. A295, or Mallinckrodt no. 1931.
- 10.10 Sulfamic acid solution, 0.4 N $\text{H}_2\text{NSO}_3\text{H}$ - Dissolve 40 g of $\text{H}_2\text{NSO}_3\text{H}$ in 1 L of reagent water.
- 10.11 Sulfuric acid - concentrated H_2SO_4 , Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.
- 10.12 Sulfuric acid, 18 N - Carefully dilute 500 mL of concentrated H_2SO_4 into 500 mL of reagent water, or use purchased 50% v/v (Fisher LabChem no. LC25640).
- 10.13 Magnesium chloride hexahydrate - $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$, Fisher no. M33, or Mallinckrodt no. 5958.

- 10.14 Magnesium chloride solution - Dissolve 510 g of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ per liter of reagent water.
- 10.15 Sodium arsenite - NaAsO_2 , Fisher no. S225I. **CAUTION:** Arsenic compounds are toxic!
- 10.16 Sodium arsenite solution, 2% (w/v) NaAsO_2 - Dissolve 2 g of NaAsO_2 into 100 mL of reagent water.
- 10.17 Stock cyanide solutions - Calibration and spiking/check standards are prepared separately from independent sources of potassium cyanide (KCN, for example Fisher no. P223I, Mallinckrodt no. 6881). **CAUTION: Poison!** Standards expire one year from date of preparation.
- Weigh ~260 mg of potassium cyanide (KCN) and 0.1-0.2 g NaOH (several pellets) into a 1-L volumetric flask, dissolve in reagent water, dilute to the mark and mix. This solution is approximately 100 ppm CN⁻. Label this solution calibration standard "A". Actual concentration is determined titrimetrically per Appendix B.
 - Weigh ~260 mg of potassium cyanide (KCN) and 0.1-0.2 g NaOH (several pellets) into a 1-L volumetric flask, dissolve in reagent water, dilute to the mark and mix. This solution is approximately 100 ppm CN⁻. Label this solution calibration standard "B". Actual concentration is determined titrimetrically per Appendix B.
- 10.18 Standard silver nitrate solution(s), 0.01-0.02 N AgNO_3 - for example, Fisher (LabChem) no. 22630, Mallinckrodt no. H394. Solutions from two sources required.
- 10.19 p-Dimethylaminobenzalrhodanine - Aldrich no. 11,458-8, or Mallinckrodt no. 2754.
- 10.20 Acetone - reagent grade, Fisher no. A18.
- 10.21 Indicator solution - Dissolve 20 mg of p-dimethylaminobenzalrhodanine in 100 mL of acetone.
- 10.22 Barbituric acid - Aldrich no. 18,569-8, or Mallinckrodt no. 2046.
- 10.23 Pyridine - $\text{C}_5\text{H}_5\text{N}$, Fisher no. P368. **CAUTION:** Strong odor.
- 10.24 Hydrochloric acid - concentrated HCl, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
- 10.25 Pyridine-barbituric acid reagent - Weigh 15 g of barbituric acid into a 1-L reagent bottle. Rinse down the sides and wet with about 100 mL of reagent water. In a fume hood, add 75 mL of pyridine, and mix thoroughly. Carefully add 15 mL of concentrated HCl and mix. Transfer to a 1000-mL volumetric flask and dilute to the mark with reagent water. Mix until all of the barbituric acid has dissolved. This solution should have a pale straw color. A dark orange or yellow indicates improper preparation and reagent needs to be re-prepared. This solution is stable for six months.
- 10.26 Sodium phosphate, monobasic, monohydrate - $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, Fisher no. S369.
- 10.27 Sodium dihydrogen phosphate buffer, 1 M - Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 1 L of reagent water. Store refrigerated.
- 10.28 Chloramine-T, Mallinckrodt no. 0614-58.
- 10.29 Chloramine-T solution - Dissolve 2.0 g of chloramine-T in 500 mL of reagent water.
- 10.30 Glacial acetic acid, CH_3COOH , Fisher no. A38.
- 10.31 Dilute acetic acid - Dilute 1 mL of glacial acetic acid to 100 mL with reagent water.

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

- 11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) *before beginning the analysis*.

11.2 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.2.1 For Method Blanks:

- Liquid samples - Aliquot 250 mL of reagent water into a clean 500-mL round bottom flask.
- Solid samples - Weigh 10 g of clean sand (20 g for reactive cyanide) into a clean 500-mL round bottom flask. Add 250 mL of reagent water.

11.2.2 For Laboratory Control Samples (samples contain approximately 400 ppb CN⁻).

- Liquid samples - Aliquot 250 mL of reagent water into a clean 500-mL round bottom flask. Accurately aliquot 1.0 mL of spiking standard 'B' into the flask.
- Solid samples - Weigh 10 g of clean sand (20 g for reactive cyanide) into a clean 500-mL round bottom flask. Add 250 mL of reagent water. Accurately aliquot 1.0 mL of spiking standard 'B' into the flask.

11.2.3 For Test Samples:

- Aqueous liquids - A representative 250 mL aliquot of sample is placed into a clean 500-mL round bottom flask. (If high cyanide content is expected, a proportionally smaller sample can be used. Bring the total volume to 250 mL with reagent water.)
- Non-aqueous liquids - Transfer a representative 25 g portion of well mixed sample into a clean 500-mL round bottom flask. Add 225 mL of reagent water to the flask.
- Mixed liquids (aqueous/non-aqueous) - The sample should be well mixed before pouring a representative aliquot. The analyst should use his/her own judgment in determining the proper aliquot size so as not to exceed 20% (50 mL) of non-aqueous portion of sample. If less than 250 mL is used, reagent water is added to bring the total volume to 250 mL.
- Solid samples - A representative 10 g portion of sample is weighed into a clean 500-mL round bottom flask. Use 20 g of sample for reactive cyanide determinations. Mixed solids may require particle size reduction to assure a homogeneous sampling of all solids in the sample. Add 250 mL of reagent water to the flask. (If high cyanide content is expected, a proportionally smaller sample can be used.)

11.2.4 For Matrix Spike Samples (samples have approximately 400 ppb CN⁻ added):

- Liquid samples - Measure two additional 250 mL aliquots of one sample, making sure to sample as homogeneous a mixture as possible. Accurately aliquot 1.0 mL of spiking standard "B" into the replicate samples, and mark them as MS and MSD.
- Solid samples - Weight two additional aliquots of one sample, making sure to sample as homogeneous a mixture. Add 250 mL of reagent water to each flask. Accurately aliquot 1.0 mL of spiking standard "B" - into the replicate samples, and mark them as MS and MSD.

- 11.2.5** Add stirring bars to samples for reactive cyanide determinations (proceed to section 11.5).
Add several boiling chips to samples for distillation (proceed to section 11.3).

NOTE: Samples for total and amenable cyanide determinations must be screened for sulfide and oxidants!

11.3 SAMPLE SCREENING AND PRE-TREATMENTS**11.3.1 Sulfide:**

- Screening is performed by placing several drops of a water sample or of the soil/water slurry on a strip of lead acetate paper which has been moistened with dilute acetic acid. A blackening of the paper indicates the presence of sulfides, and the sample must be treated prior to distillation.
- Pre-treat for sulfides by adding 25 mL of bismuth nitrate solution to the sample and mixing for 5 minutes before starting distillation.

11.3.2 Oxidants:

- Screening is performed by placing several drops of a water sample or of the soil/water slurry on a strip of KI starch paper. A darkening or blue color of the paper indicates the presence of chlorine or other oxidants, and the sample must be treated prior to distillation.
- Pre-treat for oxidants by adding small amounts of ascorbic acid to the sample until a negative result is obtained for the KI-starch paper test. Then add an additional ~0.5 g of ascorbic acid.

- 11.3.3 Samples screened for sulfides and oxidants are now ready for distillation and/or pre-treatment for cyanide amenable to chlorination (sections 11.4 and 11.5).

11.4 CHLORINATION OF SAMPLES

This treatment only for samples of cyanides amenable to chlorination.

NOTE: This procedure must be performed under amber or reduced lighting. Potassium ferricyanide may decompose under fluorescent lighting or sunlight, producing a positive result for cyanide amenable to chlorination.

- 11.4.1 Prepare two identical replicate samples for total cyanide. Reserve one replicate for a normal total cyanide analysis.
- 11.4.2 To the other replicate, in a hood, add small amounts of a 5% calcium hypochlorite solution to the sample while stirring on a magnetic stir plate until an excess of hypochlorite is present, as indicated by a positive KI-starch paper test.
- 11.4.3 Test the sample every ten minutes and maintain an excess of hypochlorite on the sample for one hour.
- 11.4.4 Add 1 mL portions of 0.1 N sodium arsenite solution until KI-starch paper indicates no residual chlorine. Add an additional 5 mL of 0.1 N sodium arsenite solution to ensure an excess of reducing agent.
- 11.4.5 Samples screened for oxidants, sulfides, and treated for amenable cyanides are now ready for distillation (section 11.5).

11.5 DISTILLATION PROCEDURE

- 11.5.1 Assemble each digestion unit in accordance with Figure 1.
- 11.5.2 Aliquot 50 mL of 1.25 N NaOH into each scrubber bottle, and add enough reagent water to cover the fritted glass bubbler on the end of the stem. Close the stopcock valve on the adapter.
- 11.5.3 When all scrubbers have been prepared, switch on the vacuum pump and adjust the stopcock valve on each set-up to allow a slow stream of air to pass through the system. Adjust the valve so that roughly two bubbles per second enter the 500 mL digestion flask through the end of the tube funnel.
- 11.5.4 Add distillation reagents:
- For total and amenable cyanide only: 25 mL of sulfamic acid solution to each sample through the tube funnel. Allow to mix for three minutes minimum.
 - 50 mL of 18 N H₂SO₄ (25 mL for reactive cyanide) to each sample.
 - For total and amenable cyanide only: 20 mL of 2.5 M MgCl₂ solution to each sample.
- 11.5.5 For total and amenable cyanide only, distill the samples (for reactive cyanide, stir the samples at room temperature and allow air flow to continue for 30 minutes):
- Switch on heating mantles and set to high.
 - Note the time that each sample begins boiling to the nearest 5 minute interval, and note on the flask with a marking pen.
 - Continue refluxing for one hour. Turn off mantle(s) and continue the airflow for at least 15 minutes.

- Allow the boiling flask to cool, dislodge the tube funnel stopper and close the vacuum valve.

11.5.6 Quantitatively transfer the scrubber solutions into clean 250-mL volumetric flasks and dilute to the mark with reagent water. The distillates are now ready for automated (LACHAT) or manual colorimetric (Milton-Roy SPEC 20) analysis.

NOTE: If samples are not to be run on the same day distilled, the distillates are stored in the refrigerator, or transferred to plastic sample cups and stored refrigerated.

11.6 PREPARATION OF CALIBRATION AND CHECK STANDARDS

11.6.1 Calibration standards are prepared by serial dilutions of stock standard "A". Note that final concentrations of the standards depend upon the concentration of the calibration source standard as determined titrimetrically (Appendix B). * (Sodium hydroxide is added to each standard to matrix match the standards with the distillates.) Prepare standard set per Table 1.

Table 1. Preparation of Calibration Standards.				
Standard Level	Volume Stock Standard (mL)	Final Volume (mL)	Volume 1.25 N NaOH (mL)	Approx. CN ⁻ Concentration (ppb)
A	1.0	100	20	1000
B	0.5	100	20	500
C	0.2	100	20	200
D	0.1	100	20	100
E	0.05	100	20	50
F	0.025	100	20	25
G	0.010	100	20	10
H	0.00	100	20	0

11.6.2 Check Standard - A Check Standard is prepared fresh daily. The check standard is prepared by aliquoting 0.5 mL of Spiking Source Standard "B" into a 100-mL volumetric flask, adding 20 mL of 1.25 N NaOH, diluting to the mark with water, and mixing. This check standard contains approximately 500 ppb cyanide. Reserve the previous check standard as it will also be evaluated with the run as the "old check standard".

NOTE: At client request, high and low standards may be distilled along with samples. The concentrations of the distilled check standards should be $\pm 10\%$ of the undistilled standards.

11.7 OPERATION OF THE LACHAT ANALYZER

11.7.1 Power up the Lachat analyzer in accordance with the manufacturer's instructions. **Allow the system to warm up at least 15 minutes.**

11.7.2 Install the cyanide manifold, sample loop, and filter, making sure that all connections have been made and properly tightened.

11.7.3 Place the reagent uptake tubes in their appropriate reagent bottles and prime the system while checking for leaks.

- 11.7.4 Pour an aliquot of each Calibration Standard (A-H) into 6-mL disposable culture tubes and place in the corresponding sampler positions (see Table 2).

Table 2. Positions of Samples in the Analyzer.					
Position	Sample	Position	Sample	Position	Sample
1	Blank	5	High Cal Std	9	Matrix Spike
2	Blank	6	Blank	10	Matrix Spike Duplicate
3	Old Check Std	7	Method Blank	11	Matrix Sample
4	New Check Std	8	LCS	12	Blank

- 11.7.5 The remaining samples from the batch are loaded into the sampler with a Check Standard and Calibration Blank every ten or less samples, including the QC spikes and samples. Each analytical run must end with the analysis of a blank and check standard.
- 11.7.6 Select "ANALYSIS METHOD SELECT AND DOWNLOAD" and select the "CYANIDE - NO BOUND" program. The system will now call up its operating parameters and set a baseline. Observe this baseline on the instrument screen. If it appears unstable or drifts upward or downward, allow more warm up time for the instrument. Other baseline anomalies may be indicative of other system problems and the operations manual should be referenced and the Department Manager notified.
- 11.7.7 After the baseline has stabilized, select "SUBMIT" and "CALIBRATE NOW". The system will re-zero the baseline and perform a calibration. The data system will perform a linear least squares regression analysis based on the segments selected. All usable segments must have an R^2 fit of .9950 or better to be deemed acceptable. If the calibration fails to meet this criteria, the system will indicate this and require analyst review of the calibration prior to acceptance. The reason for the calibration failure should be determined and the calibration re-run if necessary.
- NOTE:** It is recommended that the analyst review the calibration data before running samples, even if the calibration has passed. A good mathematical curve fit might not produce accurate results near the detection limit/baseline, and the curve might necessarily need to be re-run even though the fit was acceptable due to anomalous baseline response.
- 11.7.8 After the calibration has been passed and accepted by the analyst, select "IDENTIFICATION". Remove the default end run marker (..) by overwriting with two spaces. Escape to exit.
- 11.7.9 Select "RUN CURRENT TRAY". Follow the instructions to initiate the run using "Y" for start tray, "96" for number of samples, and "1" for tray start position.
- 11.7.10 The analyzer will run the samples and determine the cyanide concentrations using the newly created calibration curve. For this data to be acceptable, the criteria in Table 3 must be met.

NOTE: Batch data not within specified limits may be re-analyzed later in the run. The ICB, ICV, and High Calibration Standard must pass to continue with the run. Any dilution factors used on samples are to be noted in the log book and on the run sheet. Samples falling outside the high end of the curve may be diluted with 0.25 N NaOH and re-run.

In addition, if the old versus new check standards fail to meet the above criteria and fresh working standard preparation does not resolve the discrepancy, the stock standards should be re-titrated to verify the cyanide concentration of BOTH calibration and spiking standard. If the concentration has changed, the standards and logs must be updated as if a new preparation had been performed, but using the original expiration date(s).

**Table 3.
Run Data Acceptance Criteria.**

Sample Type	Acceptance Parameter	Action Upon Parameter Failure
Blanks	< Reporting D.L. or <M.D.L (spec case)	Re-analyze blank - if still fails, recalibrate and re-run - if still fails prepare fresh, re-cal and re-run
Old Check Std	± 10 % of known value	Re-analyze check std - if still fails, recalibrate and re-run - if still fails prepare fresh and re-run
New Check Std	± 10 % of known value	Must be within 10 % of old check std, else prepare fresh calibration standards and re-calibrate
High Cal Std	± 10 % of known value	Re-analyze standard - if still fails, recalibrate and re-run - if still fails prepare fresh, re-cal and re-run
Method Blank	< Reporting D.L. or <M.D.L (spec case)	Re-analyze - if contamination is suspected, redigest - if proven, redigest batch if hits
LCS	within established control limits or 85-115	If out of control, re-analyze - if still fails, redigest - if still fails, re-cal - if still fails, redigest set
Matrix Spike	within established control limits and RPD	Evaluate data, must obtain managerial approval to report , initiate corrective action
Matrix Spike Duplicate	within established control limits and RPD	Evaluate data, must obtain managerial approval to report , initiate corrective action
Sample Results	within 10% of calibration curve high standard	Dilute sample with cal blank solution and re-run
Continuing Check Stds	± 20 % of known value	Correct problem, reanalyze all samples since last good CCV - if fails, re-cal and re-run
Continuing Blanks	< Reporting D.L. or <M.D.L (spec case)	Correct problem, reanalyze all samples since last good CCB - if fails, re-cal and re-run

11.8 CALCULATIONS

After a run has been completed and all of the verification standards are in control, the data may be calculated and reported.

11.8.1 Liquid Samples:

$$\text{mg CN / L} = \frac{\text{Lachat result} \times \text{dilution factor} \times \text{final distillate volume (mL)}}{\text{initial sample volume (mL)} \times 1000}$$

11.8.2 Solid Samples:

$$\text{mg CN / L} = \frac{\text{Lachat result} \times \text{dilution factor} \times \text{final distillate volume (mL)}}{\text{initial sample weight (g)} \times 1000}$$

(The dilution factor is 1, unless additional dilution of the sample was done at the instrument.)

11.8.3 For amenable cyanide:

Cyanide amenable to chlorination =

$$\text{Total cyanide (untreated sample)} - \text{Total cyanide (treated sample)}$$

NOTE: The cyanide amenable to chlorination test is subject to a matrix interference in the presence of iron-cyanide complexes. If the result of the treated sample is higher than the total cyanide result but is within precision limits for the method, the result should be reported as "no determinable quantities of cyanide amenable to chlorination". If the difference is greater than precision limits, the nature of the interference should be determined and accounted for in the reported result.

11.8.4 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.8.5 Relative Percent Difference (%RPD) for duplicate analyses:

$$\% \text{RPD} = \frac{|\text{Conc. of 1}^{\text{st}} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of 1}^{\text{st}} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be used who may be unsure of the instrumentation and a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

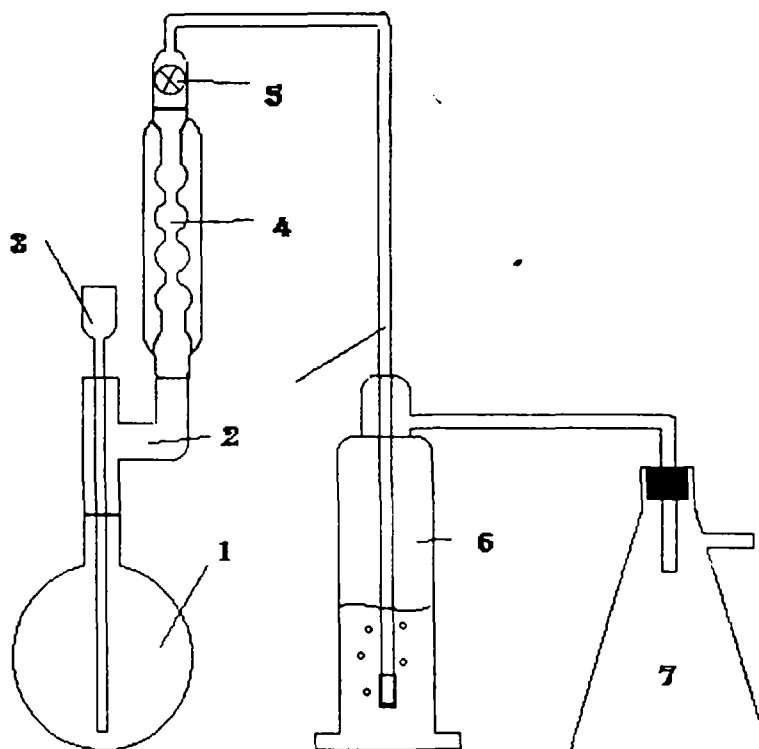
13.0 REFERENCES

- 13.1 Method 335.4: Cyanide, Total (Semi-automated colorimetry).
- 13.2 Methods 4500-CN: A, B, C, E, G, and I: Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
- 13.3 Methods SW-846 - 9010B (Revision 2): Total and Amenable Cyanide, Distillation; and 9012A (Revision 1): Total and Amenable Cyanide (Automated Colorimetric, with Off-line Distillation).
- 13.4 Methods SW-846 (Revision 2) - Chapter Seven: Characteristics Introduction and Regulatory Definitions, Section 7.3.3: Reactive Cyanide (pages 4-8).
- 13.5 Great Lakes Analytical Quality Assurance Program Manual.
- 13.6 Great Lakes Analytical Chemical Hygiene Plan.
- 13.7 Great Lakes Analytical SOP for Login Department.
- 13.8 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

See the Great Lakes Analytical Quality Assurance Program Manual

Figure 1.
Apparatus for cyanide distillation.



1. 500-mL Round-bottom flask
2. Claissen adapter
3. Thistle top tube funnel
4. Allihn condenser
5. Stopcock/connecting tubing
6. Gas scrubber/absorber
7. Vacuum trap (outlet to vacuum pump)

APPENDIX A.**EXAMPLES OF DOCUMENTATION SHEETS.**

- A.1 Log book cover page.
- A.2 Reagent preparation log sheet - 10.17: Stock calibration/reference standards.
- A.3 Reagent preparation log sheet - 10.10: Sulfamic acid solution.
- A.4 Reagent preparation log sheet - 10.14: Magnesium chloride solution.
- A.5 Reagent preparation log sheet - 10.27: Phosphate buffer solution.
- A.6 Reagent preparation log sheet - 10.25: Pyridine-barbituric acid reagent.
- A.7 Cyanide determinations run log.

Book nnn

**TOTAL CYANIDE
(TOTAL AND AMENABLE CYANIDES)**

GLA 335.4 BG

**PREPARATION AND ANALYSIS
LOG BOOK**

Date Started: _____

Date Stopped: _____

This is a controlled document (properly identified and logged):

QA Manager: _____ Date: _____

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REAGENT PREPARATION LOG SHEET

GLA 335.4 BG CYANIDE: STOCK CALIBRATION/REFERENCE STANDARDS

Preparation of Cyanide Stock Standard Solutions (10.17)					
Weigh ~260 mg of KCN and 0.1-0.2 g NaOH (several pellets) into a 1-L volumetric flask, dissolve in reagent water, dilute to the mark and mix. This solution is approximately 100 ppm CN ⁻ . Label the solution calibration standard "A" or "B" as appropriate. Actual concentrations are determined titrimetrically per Appendix B.					
Reagent	Weight (g)	Manufacturer	Lot No.	GLA No.	Rec'd Date
KCN "A"					
KCN "B"					
NaOH					
Silver nitrate	Concentration (N)				
- #1		Mallinckrodt			
- #2		Ricca			
Analyst/date:					

Titration of Cyanide Stock Standard Solution "A"				
Date	Initials	Silver Nitrate	Volume Titrant (mL)	Calculated Cyanide (mg/L)
		#1		
		#1		
		#1		
		#2		
		#2		
		#2		
Average cyanide concentration =				

GLA Code No.:	Exp. Date:
---------------	------------

Titration of Cyanide Stock Standard Solution "B"				
Date	Initials	Silver Nitrate	Volume Titrant (mL)	Calculated Cyanide (mg/L)
		#1		
		#1		
		#1		
		#2		
		#2		
		#2		
Average cyanide concentration =				

GLA Code No.:	Exp. Date:
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REAGENT PREPARATION LOG SHEET

GLA 335.4 BG CYANIDE: REAGENTS FOR DISTILLATIONS

Preparation of Sulfamic Acid Solution (10.10)									
Dissolve 40 g of sulfamic acid ($\text{H}_2\text{NSO}_3\text{H}$) in 1 L of reagent water.									
	Reagent	Manuf.	Lot No.	GLA No.	Rec'd Date	Weight (g)	GLA Code No.	Expiry	Analyst Initials/Date
1	Sulfamic acid								
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

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REAGENT PREPARATION LOG SHEET

GLA 335.4 BG CYANIDE: REAGENTS FOR DISTILLATIONS

Preparation of Magnesium Chloride Solution (10.14)									
Dissolve 510 g of magnesium chloride (MgCl_2) in 1 L of reagent water.									
	Reagent	Manuf.	Lot No.	GLA No.	Rec'd Date	Weight (g)	GLA Code No.	Expiry	Analyst Initials/Date
1	MgCl_2								
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

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REAGENT PREPARATION LOG SHEET

GLA 335.4 CYANIDE: REAGENTS FOR DISTILLATIONS

Preparation of Phosphate Buffer Solution (10.27)									
Dissolve 138 g of sodium phosphate dibasic (NaH_2PO_4) in 1 L of reagent water. Store refrigerated.									
	Reagent	Manuf.	Lot No.	GLA No.	Rec'd Date	Weight (g)	GLA Code No.	Expiry	Analyst Initials/Date
1	NaH_2PO_4								
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

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REAGENT PREPARATION LOG SHEET

GLA 335.4 CYANIDE: REAGENTS FOR ASSAY

Preparation of Pyridine-Barbituric Acid Reagent (10.25)							
Weigh 15 g of barbituric acid (A) into a 1-L reagent bottle. Rinse down the sides and wet with about 100 mL of reagent water. In a fume hood, add 75 mL of pyridine (B), and mix thoroughly. Carefully add 15 mL of concentrated HCl (C) and mix. Transfer to a 1000-mL volumetric flask and dilute to the mark with reagent water. Mix until all of the barbituric acid has dissolved. This solution is stable for six months.							
Reagent		Manuf.	Lot No.	GLA No.	Rec'd Date		
A-1	Barbituric acid						
-2							
B-1	Pyridine						
-2							
C-1	conc. HCl						
-2							

	Barb. Acid (A)	Weight A (g)	Pyridine (B)	conc. HCl. (C)	GLA Code No.	Expiry	Analyst Initials/Date
1	A-1		B-1	C-1			
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							

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GLA 335.4 CYANIDE RUN LOG

Page n of N

Batch No.:				Matrix:			
		Analyst	Date	Spiking/Cal. Standard		Conc.	Expiry
Sample Prep.:				GLA-			
Sample Analysis:				GLA-			
Carrier:		Buffer:		Reagent:		Chlor-T:	
	Client GLA Sample ID	Amount used (mL/g)	Dilution Factor	Lachat Reading	Lachat Result	Calculated Result (mg/L CN)	Recovery (%)
1	MB						
2	LCS						
3	MS						
4	MSD						
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							

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APPENDIX B.**DETERMINATION OF CYANIDE CONCENTRATIONS BY TITRATION.**

- B.1 Cyanide in solution forms a complex with added silver ion. After all cyanide becomes bound, excess silver ion is detected by the silver sensitive indicator p-dimethylaminobenzalrhodanine, which changes from a yellow to a salmon color.
- B.2 Aliquot 50 mL of the approximately 100 ppm cyanide stock solution to a beaker suitable for titration, add 5 mL of 1.25 N NaOH, a stir bar, and 0.5 mL (10 drops) of indicator solution. Provide moderate stirring.
- B.3 Place silver nitrate (AgNO_3) titrant #1 into a 10-mL buret, and titrate the diluted cyanide solution to the first change in color from a canary yellow to a salmon hue. Record the volume used.
- B.4 Prepare and titrate 5 additional aliquots of cyanide stock standard solution, 2 using titrant #1 and 3 with titrant #2.
- B.5 Prepare a blank by adding 5 mL of 1.25 N NaOH to 50 mL of reagent water. Add 0.5 mL (10 drops) of indicator solution. Plate on the magnetic stirrer and titrate. Record the volume of titrant used.
- B.6 Calculate the concentration of cyanide in the stock standard from each titration by:

$$\text{mg CN/L} = \frac{(A - B) \times \text{normality titrant} \times 10}{0.0192}$$

Where:

A = volume of titrant used for cyanide stock standard solution.

B = volume of titrant for blank.

10/0.0192 is the conversion factor for normality silver nitrate to mg/L (ppm) cyanide, and accounting for the volume of cyanide stock standard used.

- B.7 Calculate the average concentration determined.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

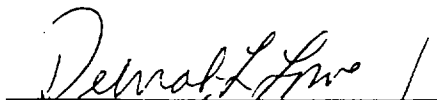
SYNTHETIC PRECIPITATION LEACHING PROCEDURE (SPLP)

GLA 1312 BG

Revision 1.0

Approved By:

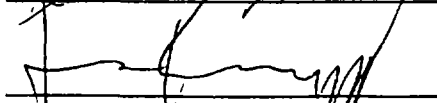
Department Manager:



Date:

7/15/99

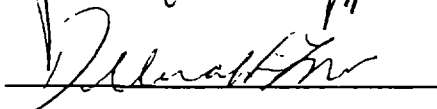
Quality Assurance Manager:



Date:

7/14/99

Laboratory Director:



Date:

7/15/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for performing the synthetic precipitation leaching procedure (SPLP). This SOP is an interpretation of EPA Method SW-846 no. 1312. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to liquid, solid, and multi-phasic samples.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

The synthetic precipitation leaching procedure (SPLP) is designed to simulate the leaching wastes will undergo when exposed to rain water. Samples are extracted with sulfuric acid/nitric acid solution at pH 4.2 or 5.0 (water for samples that may contain cyanide and for analysis of volatile compounds) for 18 ± 2 hours. The specific extraction fluid used depends upon the source of the sample (east or west of the Mississippi River). This SPLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multi-phasic samples.

- 2.1 Liquid samples (*i.e.* samples containing less than 0.5% dry solid material) are filtered through a 0.6 to 0.8 μ m glass fiber filter to produce the SPLP extract.
- 2.2 For samples containing more than 0.5% solids, the liquid (if any) is separated from the solid phase and stored for later analysis. The particle size of the solid phase is reduced if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the sample. Zero-headspace extractors (ZHE) are used when testing for volatile analytes. (See Appendix A for a list of volatile compounds.) Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 - 0.8 μ m glass fiber filter.
- 2.3 If compatible (*i.e.* multiple phases will not form on combination), the initial liquid phase of the sample is added to the liquid extract, and analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous components. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

4.0 INTERFERENCES

- 4.1 Potential interferences that may be encountered during analyses are discussed in the individual analytical methods.
- 4.2 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly. Periodic cleaning of sample preparation and analysis areas will be performed. Deionized water used for the extraction of volatile analytes must be boiled for a minimum of one hour prior to use to remove low level contaminants.

5.0 RECORD KEEPING

- 5.1 Each analyst is responsible for keeping accurate and up-to-date records of all SPLP extractions performed.
- 5.2 SPLP Logbooks:

Logbooks will be maintained for all SPLP extractions. Examples of sheets for these logbooks can be found in Appendix B. All information regarding samples processed in the lab will be entered into these books. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Analyst's signature and date/times of extraction
- All readings, including volumes and weights of materials
- Sample matrix type
- Final extraction volume and pH
- Initial sample weight used
- LCS and matrix spike information

This logs should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

- 5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 METHOD BLANK

A minimum of 1 blank (using the same extraction fluid and vessel type as the samples) must be analyzed for every batch of extractions that have been conducted in an extraction vessel. Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks should produce a concentration below the reporting limit (e.g. PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.2 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD)

With each batch of 20 samples or less, a matrix spike and matrix spike duplicate is prepared using aliquot volumes from one of the samples in the batch. More specific discussion on acceptance criteria and spike concentrations can be found in the corresponding analysis SOPs. Discussion of how the spike is added to the sample can be found in section 11.2.8.

6.3 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (e.g. a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedures for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "SPLP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

9.0 EQUIPMENT

9.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessels in an end-over-end fashion at 30 ± 2 rpm (see Figure 1). The rotation rate of each device should be checked monthly by placing a highly-visible marker on the device and counting the number of revolutions over a 60 second period. Some examples of suitable apparatus are: Analytical Testing & Consulting Services no's. DC20x and DC24C, Associated Design & Manufacturing Company no's. 3740-nn-BRE, Environmental Machine & Design no. 08-00-00, IRA Machine Shop & Laboratory no. 011011, Lars Lande Manufacturing no. 10VRE, and Millipore Corp. no's. 4-ZHE and YT310RAHW.

9.2 Zero-headspace extraction vessels (ZHE): These devices are only used when the sample is being tested for the mobility of volatile analytes. The ZHE (see Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel. The vessels have an internal volume of 500-600 mL, and are equipped to accommodate a 90-110 mm filter. The devices contain VITON o-rings which should be replaced when worn. Some examples of suitable ZHE devices are: Analytical Testing & Consulting Services no. C102, Associated Design & Manufacturing Company no. 3745-ZHE, Environmental Machine & Design no. VOLA-TOX1, Lars Lande Manufacturing no. ZHE-11, and Millipore Corp. YT30090HW.

- The components of the ZHE extractors which will contact the samples (especially the viton rubber components) should be heated in a 105°C oven for a period of one hour and allowed to cool completely before assembling the extractors.
- For the ZHE to be acceptable for use, the piston within the device should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the o-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for SPLP analyses and the device repaired or discarded.
- The ZHE devices should be checked for leaks after each extraction. If the devices contain built-in pressure gauges, pressurize to 50 psi, allow to stand for 1 hour, and recheck the pressures. If the devices do not have built-in pressure meters, pressurize to 50 psi, submerge in water, and check for air bubbles escaping from any of the fittings. If pressure is lost, check all fittings, inspect (and replace if necessary) the o-rings, and then retest the device. If leakage problems cannot be solved, the device cannot be used.
- Some ZHE devices use gas pressure to actuate the ZHE piston, while others use mechanical pressure. Whereas the volatiles SPLP procedure refers to pressure in psi, the pressures applied to mechanically actuated pistons are measured in torque (inch-pounds). Refer to the manufacturer's instructions for the proper conversion from psi to inch-lbs.

9.3 Bottle extraction vessels: When sample is being evaluated for non-volatile analytes, bottles with sufficient capacity to hold samples and appropriate volumes of extraction fluid are needed. (Headspace is allowed for non-volatile SPLP.)

The extraction bottles may be constructed from various materials, depending upon the analytes to be analyzed, and the nature of the sample. Polytetrafluoroethylene (PTFE, Teflon) plastic or fluorinated HDPE bottles must be used if organics are to be investigated. Borosilicate glass bottles should be used instead of other types of glass bottles when inorganics are of concern. Bottles may come from the manufacturer washed and ready for metal analyses. Some examples of suitable bottles are: Eagle-Picher 500-mL and 2-L natural HDPE wide mouth jars with PP lids - level 1 - no's. 151-500W/WM and 150-02W/WM, and Nalge 2-L fluorinated (FLPE) bottles no. 2097-0005.

9.4 Filtration devices: Filtrations should be performed in a hood. When the sample is to be evaluated for volatile components, the ZHE vessel is used for filtration. (Note: If it is suspected that the glass fiber filter has ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.) Otherwise, any filter holder capable of supporting a glass fiber filter and withstanding the pressure required for separations may be used. These devices should have a minimum internal volume of 300 mL and accommodate a minimum filter size of 47 mm - devices

capable of 1.5 L volume using 142 mm diameter filters are recommended. Vacuum filtration can only be used for samples with low solids content (e.g. < 10%), and for highly granular, liquid-containing samples. All other types of samples should be filtered using positive pressure filtration. Some examples of suitable filter holders are: Micro Filtration Systems no. 302400, Millipore Corp. no. YT30142HW, and Nucleopore Corp. no. 425910. (Note: Extraction vessels and filtration devices must be made of inert materials which will not leach or absorb sample components. Glass, PTFE, and stainless steel 316 equipment may be used for organic and inorganic component analyses. High density polyethylene - HDPE, polypropylene - PP, and polyvinyl chloride - PVC - equipment may be used for metals.)

- 9.5 Filters: Borosilicate glass fiber, without binder materials, effective pore size 0.6 to 0.8 μm . Acid-washed filters (1 N nitric acid followed by reagent water, or purchased) must be used for metal analyses. Glass fiber filters are fragile and should be handled with care. Some examples of suitable filters are: Gelman Science no. 66257, Micro Filtration Systems GF75, Millipore Corp. no. AP40, Nucleopore Corp. no. 211625, and Whatman no. GFF, acid-washed 1810-142.
- 9.6 ZHE extract collection devices: TEDLAR® bags are used to collect the initial liquid phase and the final extract using ZHE devices.
- If the sample contains an aqueous liquid phase or if a sample does not contain a significant amount of non-aqueous liquid (i.e. < 1% of total), the TEDLAR bag or a 600-mL syringe may be used to collect and combine the initial liquid and solid extract.
 - If a sample contains a significant amount of non-aqueous liquid in the initial liquid phase (i.e. > 1% of total), the syringe or the TEDLAR bag may be used for both the initial liquid/solid separation and the final extract filtration. However, analysts should use one or the other, not both.
 - If the sample contains no initial liquid phase (i.e. 100% solids) or has no significant solid phase (i.e. 100% liquid), either a TEDLAR bag or a syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.
- 9.7 ZHE extraction fluid transfer device: Any device capable of transferring extraction fluid into the ZHE devices without changing the nature of the extraction fluid (e.g. positive displacement or peristaltic pump, gas-tight syringe, pressure filtration unit).
- 9.8 Laboratory balance, calibrated, capable of weighing up to 1 kg (?) with 0.01 g accuracy (all weight measurements are to be within ± 0.1 g).
- 9.9 pH Meter and probe - standardized and accurate to ± 0.05 units at 25°C.
- 9.10 Thermometer, capable of storing minimum and maximum temperatures over the range of 15-30°C (Fisher no. 15-077-17B, or equivalent).

10.0 STANDARDS AND REAGENTS

- 10.1 Reagent water - ASTM Type II Water (DI water) - no interferants at or above the detection limits for the methods. Reagent water for volatile extractions may be prepared passing DI water through a carbon filter, using a Millipore Super-Q system (or equivalent), and boiling for one hour.
- 10.2 Nitric acid - concentrated HNO_3 , ACS/reagent grade, **CAUTION:** Nitric acid is corrosive.
- 10.3 Sulfuric acid - concentrated H_2SO_4 , ACS/analytical reagent grade, **CAUTION:** Sulfuric acid is corrosive.
- 10.4 Sulfuric acid/nitric acid (60/40 wt% mixture): Cautiously mix 6.0 g of concentrated H_2SO_4 with 4.0 g of concentrated HNO_3 and dilute to 250ml with reagent water.
- 10.5 Extraction Fluid #1 (for samples obtained from sites east of the Mississippi River): For each liter of extraction fluid, add sulfuric acid/nitric acid mixture into 1 L of reagent water until the pH is 4.20 ± 0.05 .
- 10.6 Extraction Fluid #2 (for samples obtained from sites west of the Mississippi River): For each liter of extraction fluid, add sulfuric acid/nitric acid mixture into 1 L of reagent water until the pH is 5.00 ± 0.05 .

10.7 Extraction Fluid #3 (for cyanide and volatiles leachability): Use reagent water.

NOTE: Solutions are unbuffered and exact pH may not be attained.

NOTE: Extraction fluids should be monitored for impurities. The pH should be checked prior to use to ensure that they were prepared correctly. If impurities are found, or the pH is not within specifications, the fluid is discarded and fresh extraction fluid prepared. Also see Appendix B for example of logsheet for preparation of extraction fluids.

11.0 PROCEDURE

NOTE: Record all pertinent sample information in the logbooks. See Appendix C for guidelines for sample collection, preservation, and handling.

11.1 PRELIMINARY EVALUATIONS

Preliminary SPLP evaluations may be performed on a minimum 100 g aliquot of sample. This aliquot may not actually undergo SPLP extraction. These preliminary evaluations may include:

- determination of the percent solids (section 11.1.1);
- determination of whether the sample contains insignificant solids and therefore can be used directly for analyses, following filtration (section 11.1.2);
- determination of whether the solid portion of the sample requires particle size reduction (section 11.1.3); and
- determination of appropriate extraction fluid (section 11.1.4).

11.1.1 DETERMINATION OF PERCENT SOLIDS: Percent solids is defined as that fraction of a sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below:

- If the sample will obviously yield no liquid when subjected to pressure filtration (*i.e.* is 100% solids), proceed to section 11.1.3.
- If the sample is liquid or multi-phasic, separation of the liquid phase from the solid phase is required:
 - * Pre-weigh the filter and the container that will receive the filtrate.
 - * Assemble the filter holder and filter. Place the filter on the support screen and secure.
 - * Weigh a subsample (100 g minimum) and record the weight.
 - * Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the sample through the same filtration system.
 - * Quantitatively transfer the sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of cold sample (from refrigerator) reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature in the device before filtering.
 - * Gradually apply vacuum or gentle pressure (1-10 psi) until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute period, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (*i.e.* filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.
 - * The material in the filter holder is defined as the solid portion of the sample, and the filtrate is the liquid phase.

- * Determine the weight of the liquid phase by subtracting the weight of the filtrate container from the weight of the filtrate container from the total weight of the filtrate-filled container. Determine the weight of the solid phase by subtracting the weight of the liquid phase from the weight of the total sample used.
- * Record the weights of the liquid and solid phases. Calculate the percent solids:

$$\text{Percent solids (\%)} = \frac{\text{Weight of solid}}{\text{Total weight of sample}} \times 100$$

NOTE: If sample material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the total sample weight for the actual amount of the sample that will be filtered.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, this material may not filter. If this is the case, the material within the filtration device is considered as being solid. Do not replace the original filter with a fresh filter under any circumstances - use only one filter.

11.1.2 NON-SOLID SAMPLES: If the percent solids is less than 0.5%, then proceed to section 11.2.9 if the non-volatile SPLP is to be performed, and/or to section 11.3 (with a fresh portion of the sample) if the volatile SPLP is to be performed. If the percent solids is equal to or greater than 0.5%, then proceed to section 11.1.3 to determine whether the solid material requires particle size reduction, or perform the procedure outlined below if it is noticed that a small amount of the filtrate is entrained in wetting of the filter:

- Remove the solid phase and filter from the filtration apparatus.
- Dry the filter and solid phase at $100 \pm 20^\circ\text{C}$ until 2 successive weighings yield the same value within $\pm 1\%$. Record the final weight.
- Calculate the percent dry solids:

$$\text{Percent dry solids (\%)} = \frac{(\text{Weight of dry sample + filter}) - \text{Tared weight of filter}}{\text{Initial weight of sample}} \times 100$$

- If the percent dry solids is less than 0.5%, then proceed to section 11.2.9 if the non-volatile SPLP is to be performed, and/or to section 11.3 if the volatile SPLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the non-volatile SPLP is to be performed, return to the beginning of this section (11.1), and with a fresh portion of sample, determine whether particle size reduction is necessary (section 11.1.3).

NOTE: Caution should be taken to ensure that the subject solid will not flash or react violently upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

11.1.3 PARTICLE SIZE REDUCTION: Using the solid portion of the sample, evaluate the solid for particle size. Particle size reduction is required unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2 , or is smaller than 1 cm in its narrowest dimension (*i.e.* capable of passing through a 9.5 mm - 0.375 inch - standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the sample to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see section 11.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g. paper, cloth, and similar) materials. Actual measurement of surface area is not required, nor is recommended. For materials that do not obviously meet the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is not currently available.

11.1.4 DETERMINATION OF APPROPRIATE EXTRACTION FLUID:

For wastes and wastewater, use extraction fluid #1.

For soils, if the sample is from a site that is east of the Mississippi River, use extraction fluid #1; if the site is west of the Mississippi River, use extraction fluid #2.

For cyanide-containing wastes and/or soils, extraction fluid #3 (water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

- 11.1.5 If the aliquot of the sample used for the preliminary evaluation (sections 11.1.1 - 11.1.4) was determined to be 100% solid, then it can be used for the section 11.2 extraction (assuming at least 100 g remain), and the section 11.3 extraction (assuming at least 25 g remain). If the aliquot was subjected to the filtration procedure described in section 11.1.1, then another aliquot is used for the volatile procedure in section 11.3. The aliquot of the sample subjected to the filtration procedure in 11.1.1 might be appropriate for the section 11.2 extraction if an adequate amount of solid was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to section 11.2.10 of the non-volatile SPLP.

11.2 SPLP PROCEDURE FOR NON-VOLATILE ANALYTES

A minimum sample size of 100 g (liquid and solid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the sample, whether the initial liquid phase of the sample will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of SPLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single SPLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed, and the extracts from each combined and aliquoted for analysis.

- 11.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (i.e. is 100% solid), weigh a subsample (100 g minimum) and proceed to section 11.2.3.
- 11.2.2 If the sample is liquid or multi-phasic, liquid/solid separation is required.
- Pre-weigh the container that will receive the filtrate.
 - Assemble the filter holder and filter. Place the filter on the support screen and secure. (Filters must be acid-washed for analysis of metals - acid-washed filters may be used for all non-volatile extractions, even when metals are not of concern.)
 - Weigh a subsample (100 g minimum) and record the weight. If the sample contains less than 0.5% dry solids, the liquid portion of the sample, after filtration, is the SPLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required. For samples containing more than 0.5% dry solids, use the percent solids information to determine the optimum sample size (100 g minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the SPLP extract.
 - Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered, followed by filtration of the solid portion of the sample through the same filtration system.

agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Monitor the ambient temperature (room temperature) using a min/max thermometer (be sure to reset at start of extraction time). Ambient temperature should be maintained at $23 \pm 2^\circ\text{C}$ during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of samples (e.g. limed or calcium carbonate containing sample may evolve gases such as carbon dioxide). The extractor bottle may be periodically opened (e.g. after 15 minutes, 30 minutes, and 1 hour) and vented into a hood to relieve excess pressure.

11.2.6 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in section 11.2.2. For final filtration of the SPLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Acid-washed filters are used if evaluating the mobility of metals.

11.2.7 Prepare the SPLP extract:

- If the sample contained no initial liquid phase, the filtered material obtained from section 11.2.6 is the SPLP extract. Proceed to section 11.2.8.
- If compatible (e.g. multiple phases will not result on combination), combine the filtered liquid resulting from section 11.2.6 with the initial liquid phase of the sample obtained in section 11.2.2. This combined liquid is the SPLP extract. Proceed to section 11.2.8.
- If the initial liquid phase of the sample is not, or may not be, compatible with the filtered liquid resulting from section 11.2.2, do not combine these liquids. Analyze the liquids separately, and combine the results as the SPLP extract.

11.2.8 Following collection of the SPLP extract, the pH of the extract is determined and recorded. Immediately aliquot and preserve the extracts for analysis. The MS/MSD aliquots are prepared (spiked) prior to preservation. Aliquots for metals must be acidified with nitric acid to a pH of less than 2. If precipitation is observed upon addition of nitric acid to a small amount of the extract, then the remaining portion of the extract for metals analysis is not acidified, and the extract analyzed as soon as possible. All other aliquots must be stored under refrigeration until analyzed. The SPLP extracts will be prepared and analyzed according to the appropriate analytical methods. SPLP extracts to be analyzed for metals will be acid digested, except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the sample is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the sample is not hazardous. If individual phases are analyzed separately, determine and record the volume of the individual phases (to $\pm 0.5\%$).

11.3 SPLP PROCEDURE FOR VOLATILE ANALYTES

Zero-headspace extraction (ZHE) devices are used to obtain SPLP extracts for analysis of volatile compounds only. Extracts resulting from the use of the ZHE are not used to evaluate the mobility of non-volatile analytes (e.g. metals and pesticides).

- The ZHE device has a capacity of approximately 500 mL. The ZHE can accommodate a maximum of 25 g of solid due to the requirement to add an amount of extraction fluid equal to 20 times the weight of the solid phase.
- Charge the ZHE with sample only once, and do not open the device until the final extract has been collected. Repeated filling of the ZHE to obtain 25 g of solid is not permitted.
- Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold ($\sim 4^\circ\text{C}$) to minimize loss of volatile components.
- One of the ZHE devices in each analytical batch is used for the blank. Sequence through the devices such that each will be used for the blank.

- 11.3.1 Pre-weigh the (evacuated) filtrate collection container and set aside. If using a TEDLAR bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis.
- 11.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful to first moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements).
- 11.3.3 If the sample is 100% solids, weigh a subsample (25 g maximum), record weight, and proceed to section 11.3.5.
- 11.3.4 If the sample contains less than 0.5% dry solids, the liquid portion of sample, after filtration, is the SPLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For samples containing more than 0.5% dry solids, use the percent solids information (section 11.1.1) to determine the optimum sample size to charge into the ZHE. The recommended sample size is:
- For samples containing less than 5% solids, weigh a 500 g subsample and record the weight.
 - For samples containing greater than 5% solids, determine the amount of sample to charge into the ZHE: $Weight (g) = 25g / (\text{percent solids result, as a decimal})$. Weigh a subsample of the appropriate size and record the weight.
- 11.3.5 If particle size reduction of the solid portion of the sample is not required, proceed to section 11.3.7. Otherwise continue with section 11.3.6.
- 11.3.6 Prepare the sample for extraction by crushing, cutting, or grinding the solid portion of the sample to an acceptable surface area or particle size (see section 11.1.3). Samples and appropriate reduction equipment should be refrigerated, if possible, prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the sample is necessary, exposure of the sample to the atmosphere should be avoided to the highest extent possible.
- NOTE:** Sieving of the sample is not recommended due to the possibility that volatile components may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g. paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.
- 11.3.7 The solid phase of sample slurries does not have to settle. Do not centrifuge samples prior to filtration.
- 11.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If sample material (greater than 1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in section 11.3.4 to determine the weight of the sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device (into a hood). At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of cold sample (from refrigerator) reduces the amount of expressed liquid over what would be expected and room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the sample is 100% solid, slowly increase the

pressure to a maximum of 50 psi to force most of the headspace out of the device, and proceed to section 11.3.12.

- 11.3.9 Attach the evacuated tedlar bag to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate in any 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

- 11.3.10 The material in the ZHE is the solid phase of the sample and the filtrate is the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the SPLP extraction as a solid.

If the original sample contained less than 0.5% dry solids (see section 11.1.2), this filtrate is the SPLP extract and is analyzed directly. Proceed to section 11.3.15.

- 11.3.11 The liquid phase may now be analyzed immediately (see sections 11.3.13 - 11.3.15) or stored under refrigeration and with minimal headspace until time of analysis. Determine the weight of extraction fluid #3 to add to the ZHE:

$$\text{Weight} = 20 \times (\text{percent solids}) \times (\text{weight of sample filtered}) / 100$$

- 11.3.12 The following details how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #3 (reagent water) is used in all cases.

- With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.
- After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding should be done quickly and be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.
- Place the ZHE in a rotary agitation apparatus and rotate at 30 ± 2 rpm for 18 ± 2 hours. Monitor the ambient temperature (room temperature) using a min/max thermometer (be sure to reset at start of extraction time). Ambient temperature should be maintained at $23 \pm 2^\circ\text{C}$ during the extraction period.

11.3.13 Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by reading the gauge and quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e. no gas release observed), check the ZHE for leaking, and extract a fresh portion of sample (using another ZHE if necessary). If the pressure within the device has been maintained, the material in the extractor is separated into its component liquid and solid phases. If the sample contained an initial liquid phase, the liquid may be filtered directly into the same filtrate container holding the initial liquid phase. A separate filtrate collection container must be used if combining the liquids would create multiple phases, or there is not enough empty volume remaining within the initial filtrate collection container. Filter through a glass fiber filter using the ZHE device, as described in section 11.3.9. All extract is filtered and collected if a TEDLAR bag is used, if the extract is multi-phasic, or if the sample contained an initial liquid phase (see section 11.3.1).

NOTE: If it is suspected that the glass fiber filter has ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

11.3.14 If the original sample contained no initial liquid phase, the filtered liquid material from section 11.3.13 is the SPLP extract. If the sample contained an initial liquid phase, the initial liquid phase (section 11.3.9) and the filtered liquid material (11.3.13) are collectively the SPLP extract.

11.3.15 Following collection of the SPLP extracts, immediately prepare the extracts for analysis and store refrigerated with minimal headspace until time of analysis. The SPLP extracts are analyzed according to the appropriate analytical methods. If individual phases are analyzed separately, determine and record the volume of the individual phases (to $\pm 0.5\%$).

11.4 ANALYTICAL RESULTS

If the individual phases were analyzed separately (e.g. they are not miscible), mathematically combine the results using a simple volume-weighted average:

$$\text{Final analyte concentration} = \frac{V_1 \times C_1 + V_2 \times C_2}{V_1 + V_2}$$

where:

V_1 = volume of the first phase (in L);

C_1 = concentration of the analyte of concern in the first phase (mg/L);

V_2 = volume of the second phase (in L); and

C_2 = concentration of the analyte of concern in the second phase (mg/L).

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

13.0 REFERENCES

- 13.1 Method SW-846, 1312: Synthetic Precipitation Leaching Procedure.
- 13.2 Great Lakes Analytical Quality Assurance Program.
- 13.3 Great Lakes Analytical Chemical Hygiene Plan.
- 13.4 Great Lakes Analytical SOP for Login Department.
- 13.5 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Manual.

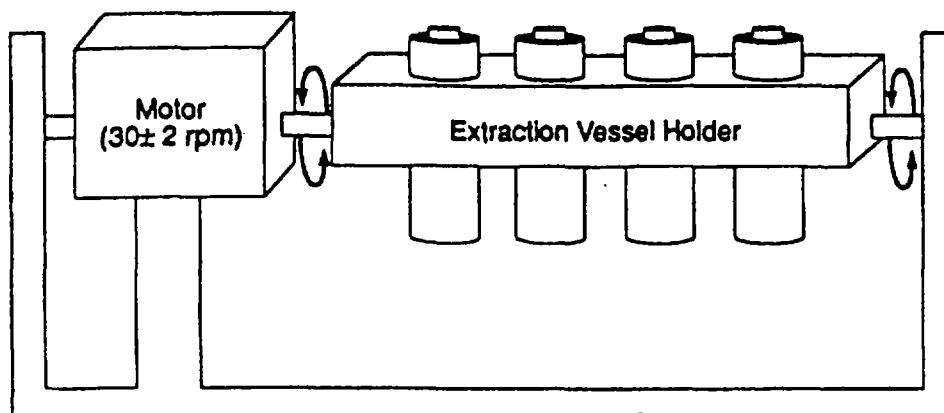


Figure 1. Rotary Agitation Apparatus

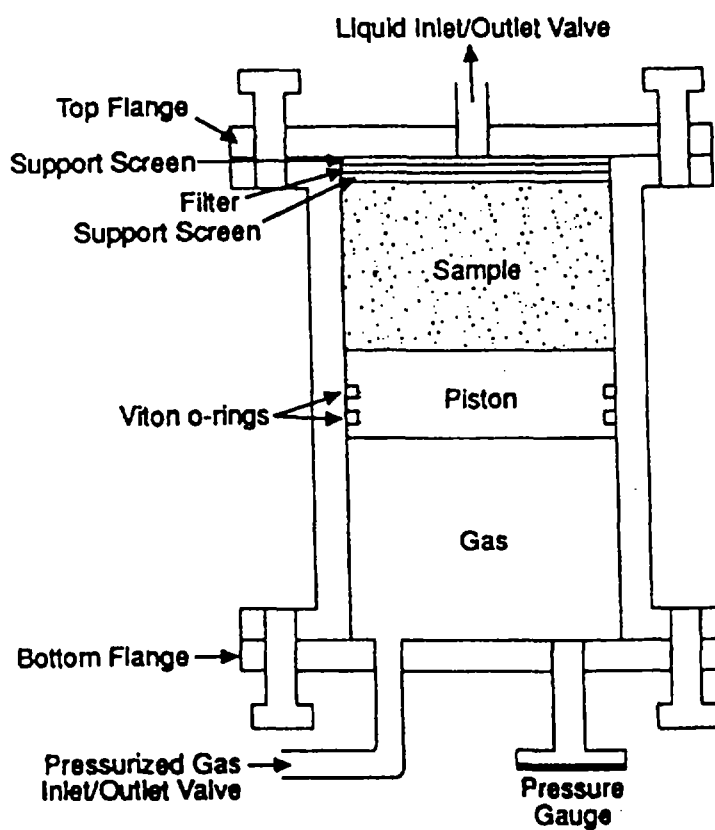


Figure 2. Zero-Headspace Extractor (ZHE)

APPENDIX A.

SPLP VOLATILE ANALYTES.

The zero-headspace extractor vessel must be used when testing for any or all of these analytes:

Acetone	
Benzene	@
n-Butyl alcohol	
Carbon disulfide	
Carbon tetrachloride	@
Chlorobenzene	@
Chloroform	@
1,2-Dichloroethane	@
1,1-Dichloroethylene	@
Ethyl acetate	
Ethyl benzene	
Ethyl ether	
Isobutanol	
Methanol	
Methylene chloride	
Methyl ethyl ketone	@
Methyl isobutyl ketone	
Tetrachloroethylene	@
Toluene	
1,1,1-Trichloroethane	
Trichlorofluoromethane	
1,1,2-Trichloro-1,2,2-trifluoroethane	
Vinyl chloride	@
Xylene	

@ = Toxicity characteristic constituent.

APPENDIX B.

EXAMPLES OF SPLP LOGBOOK SHEETS.

- B.1 *Extraction Fluid Preparation and Testing Log.*
- B.2 Solids Extraction Preparation.
- B.3 Multi-Phase and Liquid Sample Preparation.
- B.4 ZHE Extraction for SPLP Volatiles.
- B.5 Extraction Device Rotation Speed.

Appendix B1.

[illegible]

Appendix B2.

SYNTHETIC PRECIPITATION LEACHING PROCEDURE LOGSHEET												
SOLIDS EXTRACTION PREPARATION												
Great Lakes Analytical										Date:		
GLA Sample I.D.:												
A. Sample Description												
1. Solid only												
B. Percent Solid Phase												
1. Check if 100% solids												
C. Selection of Extraction Fluid (Does not apply to volatile organic components.)												
1. Particle size reduced? y/n												
2. If sample is from a site east of Mississippi River, check box, use extraction fluid #1												
3. If sample is from a site west of Mississippi River, check box, use extraction fluid #2												
4. If sample may contain cyanide or is waste or wastewater, check box, use extrctn fluid #3												
D. Sample Size for Leachables Testing												
1. Check if 100 g sample used, or enter actual weight												
E. Determination of Amount of Extraction Fluid Used												
1. 20 × sample weight												
F. Record of Extraction Data										Analyst's signature		Date
1. Extraction start time										AM / PM		
2. Extraction stop time										AM / PM		
3. Min. ambient temperature										°C		
4. Max. ambient temperature										°C		
5. pH of filtrate												
6. Volume of filtrate (mL)												

Appendix B3.

SYNTHETIC PRECIPITATION LEACHING PROCEDURE LOGSHEET										
MULTI-PHASE AND LIQUID EXTRACTION PREPARATION										
Great Lakes Analytical							Date:			
GLA Sample I.D.:										
A. Sample Description —check appropriate boxes										
1. Solids										
2. Liquid(s)										
a. Aqueous liquid (water)										
b. Non-aqueous liquid										
B. Percent Solid Phase Determination										
1. Weight of filter (g)										
2. Weight of subsample (100 g)										
3. Weight of filter container (g)										
4. Weight of filter container and filtrate (g)										
5. Weight of filtrate (g): (B.4 - B.3)										
6. Weight percent solids (wet): (B.2 - B.5) / B.2 × 100										
7. Weight of dried solids and filter (g)										
8. Weight percent solids (dry): (B.7 - B.1) / B.2 × 100										
9. Volume of initial aqueous filtrate (as applicable)										
10. Volume of initial organic filtrate (as applicable)										
C. Determination of Sample Weight Required to Support All Analyses										
NOTE: If percent solids (determined above) ≥ 75%, use 100 g, and proceed with extraction procedure.										
1. M - Metals analyses: enter 3 for Hg, 1 for no Hg										
2. SV - No. of semi-volatile analyses: 8270, 8150, 8080 (1-3)										
3. QC - Is QC to be run on this sample? (no=1, yes=3)										
4. Calculate the original sample weight required for each sample: Original sample weight (g) = (0.011) × QC × [(M × 50) + (SV × 100)] / 20 / (percent solids)										
5. Calculated sample weight to be filtered prior to extraction										
6. Actual weight of solids to be rotated/extracted (100 g min)										
Analyst's signature/date:										

Appendix B4.

Client:								
Sample Number								
A. Sample Description								
1. 100% Solids by observation								
2. ZHE NUMBER	1	2	3	4	5	6	7	8
3. Weight of waste charged to ZHE (grams)								
B. Extraction Fluid #3 addition								
1. Indicate volume of SPLP Extraction Fluid #3 (DI Water) added. (Usually 500 mL or 20 X A.3 if less than 25 g was used)								
2. Check for positive ZHE pressure								

Client:								
Sample Number								
A. Sample Description (Continued from above)								
1. 100% Solids by observation								
2. ZHE NUMBER	9	10	11	12				
3. Weight of waste charged to ZHE (grams)								
B. Extraction Fluid #3 addition: (Continued from above)								
1. Indicate volume of SPLP Extraction Fluid #3 (DI Water) added. (Usually 500 mL or 20 X A.3 if less than 25 g was used)								
2. Check for positive ZHE pressure								

C. Record of Extraction Period	Time	Analyst's signature	Date
1. Extraction Start Time	AM/PM		
2. Extraction Stop Time	AM/PM		
3. Min. ambient temperature	° C		
4. Max. ambient temperature	° C		

Appendix B5.

TCLP/SPLP Extraction Device Rotation Speed		
Unit I.D.	Speed (RPM)	Initial and Date
<i>Acceptance criteria: 28 to 32 rpm.</i>		

APPENDIX C.

SAMPLE COLLECTION, PRESERVATION, AND HANDLING.

- C.1 All samples will be collected using an appropriate sampling plan.
- C.2 The SPLP may place requirements on the minimum size of the field sample, depending upon the physical state(s) of the sample and the analytes of interest. An aliquot will be needed for the preliminary evaluation of which extraction fluid is to be used (for the non-volatile extraction procedure). Another aliquot may be needed to actually conduct the non-volatile extraction. Another aliquot may be needed for the analysis of volatile organics. Quality control measures may require additional aliquots. Further, additional sample may be useful in case the initial testing is not acceptable.
- C.3 Preservatives are not added to samples before extraction.
- C.4 Samples may be refrigerated, unless refrigeration results in irreversible physical changes to the sample. If precipitation occurs, the entire sample (including precipitate) should be extracted.
- C.5 Care must be taken to minimize the loss of volatile components when the sample is to be evaluated for volatile analytes. Samples should be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g. samples should be collected in Teflon-lined septum capped vials and stored under refrigeration; samples should be opened only immediately prior to extraction).
- C.6 SPLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs. Extracts should be preserved for other analytes according to the guidance given in the individual analytical methods. Extracts or portions of extracts for organic analyte determinations will not be allowed to come into contact with the atmosphere (e.g. no headspace) to prevent losses.
- C.7 Samples must undergo SPLP extraction within the following time periods indicated below. If sample holding times are exceeded, the values obtained will be considered minimum concentrations. Exceeding the holding time is not acceptable in establishing that a sample does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the sample exceeds the regulatory level.

MAXIMUM HOLDING TIME FOR SAMPLES				
Analytes	From field collection	From SPLP extraction	From preparative extraction	Total elapsed time
	To SPLP extraction	To preparative extraction	To determinative analysis	
Volatiles	14	n/a	14	28
Semi-volatiles	14	7	40	61
Metals, except Hg	180	n/a	180	360
Mercury	28	n/a	28	56

APPENDIX D.

METHOD OF STANDARD ADDITIONS.

- D.1 The method of standard additions requires preparing calibration standards in the sample matrix rather than in reagent water or blank solution. Four (4) identical aliquots of a sample are prepared, 3 of which contain known amounts of standard added. The first addition should be prepared so that the concentration added is about 50% of the expected concentration of the (unspiked) sample. The second and third additions should be prepared so that the concentrations added are approximately 100% and 150% of the expected concentration. All 4 aliquots are maintained at the same final volume by addition of reagent water or a blank solution. The aliquots may need further dilution to maintain the concentrations in the linear range of the analytical method.
- D.2 A graph is prepared plotting the analytical response against the concentration of standard added. Linear regression analysis on the data is performed, and the negative of the x-axis intercept is the concentration of the analyte in the unspiked sample.
- D.3 Alternatively, subtract the instrumental signal, or external-calibration-derived concentration, of the unknown (unspiked) sample from the instrument signals (or external-calibration-derived concentrations) of the spiked samples. Plot the resultant instrument signals or concentrations versus the concentrations of standard added and perform linear regression. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DIGESTION OF LIQUIDS FOR THE ANALYSIS OF METALS

GLA 3015 BG

Revision 3.1

Approved By:

Department Manager:



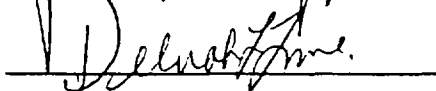
Date: 5/27/98

Quality Assurance Manager:



Date: 5/27/99

Laboratory Director:



Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the sample handling and digestion of liquids in preparation for analysis of total metals by ICP-OES and FLAA/GFAAS. This SOP is an interpretation of EPA Methods 300.7 and 300.9; Standard Methods no. 3030, Sections E, F, and K; and SW-846 no. 3015 and 3010M. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

NOTE: The digests produced using this procedure are not suitable for the analysis of mercury (Hg) or hexavalent chromium (Cr⁶⁺). Arsenic (As) and selenium (Se) cannot be analyzed by FLAA.

1.1 MATRICES

This method is applicable to aqueous samples (ground, waste, drinking waters), extracts, and other liquid materials and wastes (such as oil and grease).

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

A representative 5-100 mL portion of sample is digested with nitric acid, or nitric acid and hydrogen peroxide (for As and Se). The digestate is then refluxed with additional nitric acid (GFAAS methods, except for As and Se) or with hydrochloric acid (ICP-OES methods). Aqueous ground waters, extracts, and liquid samples are digested by either standard "hotplate" digestion methods or microwave-assisted digestion methods. Non-aqueous or high dissolved organic containing liquids are digested using the standard hotplate methods, including GLA 3010M, a modified 3010 method. Liquid matrix types include:

- Waters - ground, waste, drinking, other aqueous.
- Extracts - TCLP, SPLP, ASTM D3987-85.
- Miscellaneous - oil, grease, diesel, other.

See Appendix A for method exceptions.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 CHEMICALS SPECIFIC TO DIGESTIONS

30% Hydrogen peroxide is a strong oxidizer in the presence of acids, and can cause burns to eyes and skin. It can react violently when introduced to a sample in concentrated acid. Large volumes of hydrogen gas may be produced. Allow samples to cool thoroughly before adding hydrogen peroxide. Similarly, add concentrated nitric acid to samples carefully.

4.0 INTERFERENCES

- 4.1 Sample matrices can vary greatly, even within specific sample type groups, most notably waste sludges (for example, ground water versus tank removal waste). Any sample types exhibiting significantly different properties, such as high organic content or multi-phase samples, are to be handled as individual matrices, and appropriate matrix spikes should be produced and analyzed.
- 4.2 In the case of methods for total recoverable and/or dissolved metals, digestion is not always required. It should be noted, however, that the less intensive digestion procedure for total recoverable metals may not be sufficiently vigorous to destroy some metal complexes and may therefore give biased results.
- 4.3 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed following the procedure outlined in Appendix C. Periodic cleaning of sample preparation and analysis areas, will be performed. At least quarterly, laboratory dust wipes will be prepared and analyzed. Contamination of more than 500 µg of lead (Pb) per square foot is not permitted.

5.0 RECORD KEEPING

- 5.1 Each analyst is responsible for keeping accurate and up-to-date records of all digestions performed.
- 5.2 Digestion Log Book:

A log book will be maintained for all solid matrix types and associated digestions. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample volume used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Reviewer's signature and date
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final digestate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

- 5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (e.g. a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

8.3 METHOD DETECTION LIMIT STUDY

- 8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:
- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
 - Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's *t* value at *n*-1 degrees of freedom (3.143 for seven replicates).
- 8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.
- 8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

- 9.1 Beakers, Griffin type, 250-mL size.
- 9.2 Watch covers, ribbed, 90-mm diameter.
- 9.3 Volumetric flasks, 25-100 mL.
- 9.4 Glass funnels.
- 9.5 Filter paper - 15 cm, Whatman 41, or equivalent.
- 9.6 Sample containers, 50-100 mL capacity, metal-free.
- 9.7 Hotplate, adjustable, capable of maintaining a constant temperature for samples of 90-95°C. Monitor temperature of the hotplate by placing an Erlenmeyer flask with approximately 100 mL of cooking oil at the center of the hotplate, and reading the temperature with an ASTM thermometer positioned with the bulb against the bottom of the flask. The temperature must be at least 140°C. Record temperatures in the log book.
- 9.8 Analytical balance, calibrated - capable of weighing to nearest 0.1 g for soil/sediment/sludge samples, 0.001 g for paints.
- 9.9 Microwave digestion apparatus:
- Microwave digestion system, capable of monitoring and maintaining 175°C and/or 70 p.s.i. within digestion vessels, CEM model MDS-2100, or equivalent.
 - Lined (polyolefin) digestion vessels, 50-mL size.
 - Rupture membranes.

10.0 STANDARDS AND REAGENTS

- 10.1 Reagent water - ASTM Type II Water (DI water).
- 10.2 Nitric acid - concentrated HNO₃, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
- 10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
- 10.4 Hydrogen peroxide - 30% H₂O₂, ACS/analytical reagent grade, Fisher no. H325.
- 10.5 Spiking standards - GLA-SPK-1A, -3B, 5, and 6, Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. (Refer to Appendix B for concentrations and volumes spiked.)

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 SELECTION OF DIGESTION PROCEDURE

The appropriate method for the required metal analysis must be referenced in order to select the proper digestion procedure. There are several methods for digestions which can be selected based upon the matrix type of the sample and the type of digestion being performed. Use Table 1 to determine which method is most applicable to the samples being analyzed. The proper digestion procedure is selected from Table 2.

Table 1. Digestion Method Reference Chart.							
Analysis	Method Reference	Pre-Digestion Preparation	Microwave Digestions	Standard Digestions			Special Matrices
				ICP/FLAA	GFAA	Special	
Total Metals	SW-846	Preserve with HNO ₃ to pH <2	3051A	3010A	3020A	7060A (As) 7740A (se)	3010M for oils, gas, diesel, and waste oil sludges
	EPA		n/a	4.1.3 200.7	4.1.3 200.9	206.2 (As) 270.2 (se)	
	Std Meth		SM-3030-K	SM-3030-F	SM-3030-E		
Dissolved Metals	SW-846	Filter thru 0.45 μ filter, preserve with HNO ₃ to pH <2	3015	3010A	3020A	7060A (As) 7740A (Se)	3010M for oils, gas, diesel, and waste oil sludges
	EPA		n/a	4.4.1/4.1.3 200.7	4.1.1/4.1.3 200.9	206.2 (As) 270.2 (Se)	
	Std Meth		SM-3030-K	SM-3030-F	SM3030-E		
Total Recoverable Metals	SW-846	Preserve with HNO ₃ to pH <2	n/a	3005	n/a		3005
	EPA		n/a	4.1.4	4.4.4		4.1.4
	Std Meth		n/a	SM-3030-F	SM-3030-F		SM-3030-F

11.2 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) *before beginning the analysis*.

CAUTION: All hotplate digestions must be performed in a fume hood.

Table 2.
Procedure Selection Table.

Digestion Type	Analysis Type (1)	Analysis Method	Applicable Method(s)	Digestion Procedure
Microwave	Total Metals Dissolved Metals	Any (2)	SW-846 3015 SM-3030-K	11.4 (MIC)
Standard	Total Metals Dissolved Metals	ICP/FLAA	SW-846 3010A EPA 4.1.3 EPA 200.7 SM-3030-F	11.5 (ICP)
Standard	Total/Dissolved Except As and Se	GFAAS	SW-846 3020A EPA 4.1.3 EPA 200.9 SM-3030-E	11.6 (GF)
Standard	Total/Dissolved As and Se Only	GFAAS	SW-846 7060A (As) SW-846 7740A (Se) EPA 206.2 (As) EPA 270.2 (Se)	11.7 (AS)
Standard	Total Metals	Any (2)	3010M (3)	11.8 (NA)
Standard	Total Recoverable Metals	ICP/FLAA	SW-846 3005 EPA 4.1.4 SM-3030-F	11.9 (A)
(1) Dissolved metals require filtration at time of collection (through a 0.45 μ membrane filter) prior to preservation . Chain of custody record should be referenced to determine if sample was properly collected, filtered, and preserved. (2) Any analytical method refers to GLA routine methods : ICP, GFAAS, and FLAA. These digests are not suitable for analysis of mercury or hexavalent chromium. (3) Method 3010M is a GLA method. It is based upon the SW-846 method 3010A, but the addition of hydrochloric acid has been omitted. It is used exclusively for the analysis of metals in oils, oil waste, gas, diesel fuels, and high organic containing waters.				

11.3 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

- 11.3.1 Method blank - Aliquot 100 mL (45 mL for microwave digestion, section 11.4) of reagent water into a clean digestion vessel.
- 11.3.2 Laboratory control samples (LCS) - Aliquot 100 mL (45 mL for microwave digestion, section 11.4) of reagent water into a clean digestion vessel. Accurately aliquot 0.2 mL (0.1 for microwave) each of GLA-SPK-1A, -3B, -5, and -EM into the sample. Also add 0.2 mL (0.1 for microwave) of GLA-SPK-6 if spiking Ag and Cd at ICP levels.
- 11.3.3 Samples - Representative 100 mL (45 mL for microwave digestion, section 11.4) aliquots of samples are aliquoted into clean digestion vessels. For samples with a high solids content (> 1%), a smaller sample size should be used (record the actual volume in the log book).
- 11.3.4 Matrix spike samples - Measure two additional aliquots 100 mL (45 mL for microwave digestion, section 11.4) of one sample, with volumes similar to the test sample volume, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.2 mL each of GLA-SPK-1A, 3B, -5, and -EM into the sample. Also add 0.2 mL (0.1 for microwave) of GLA-SPK-6 if spiking Ag and Cd at ICP levels. Mark as MS and MSD.

11.4 MICROWAVE-ASSISTED DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS (MIC)

NOTE: Metal analytes for which this digestion is applicable include:

Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Ti, V, Zn.

- 11.4.1 Add 5 mL of concentrated HNO_3 to each sample. Stand for 2-10 minutes to allow any vigorous reaction to occur before the vessel is sealed.
- 11.4.2 The "control vessel" should be selected as the sample appearing to be most reactive. Load the carousel with samples and place in the microwave.
- 11.4.3 Upon completion of the microwave program, the samples are cooled until the pressure drops below 10 psi (as indicated by the instrument). The pressure sensor is carefully disconnected, temperature probe removed, and the carousel taken out of the instrument.
- 11.4.4 Each vessel is carefully vented, vent line removed, cap retightened, and shaken to mix.
- 11.4.5 Each vessel is opened and contents poured into a clean labelled sample cup. If the sample is still warm, or hot, to the touch, it should be cooled further and mixed before analysis. This can be expedited by placing samples in a refrigerator, freezer, or cold water bath for a short time. Observe the volume of each vessel. If loss of sample is apparent (e.g. volume less than 50 mL), the sample is discarded and redigested. The container should be labeled with:
 - GLA Sample I.D.
 - Matrix type
 - Date digested
 - Dilution factor (where applicable)
- 11.4.6 Samples are now ready for analysis by ICP, GFAA, or FLAA.

11.5 HOTPLATE DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS BY ICP-OES (ICP)

NOTE: Metal analytes for which this digestion is applicable include:

Al, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Ti, V, and Zn.

- 11.5.1 Add 3 mL of concentrated HNO_3 , and several boiling chips to each sample, cover with watch glasses, and mix.
- 11.5.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. Remove and cool.
- 11.5.3 Add an additional 3 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 20 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool.
- 11.5.4 Add 5 mL of reagent water and 5 mL of concentrated HCl to each sample, cover, and return to the hotplate for 15 minutes. Remove and cool.
- 11.5.5 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:
 - GLA Sample I.D.
 - Matrix type
 - Date digested
 - Dilution factor (where applicable)

11.5.6 The samples are ready for analysis by ICP (or FLAA).

11.6 DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS BY GFAA (GF)

NOTE: Metal analytes for which this digestion is applicable include:
Be, Cd, Cr (tot), Pb, Mo, Tl, and V.

11.6.1 Add 3 mL of concentrated HNO_3 , and several boiling chips to each sample, cover with watch glasses, and mix.

11.6.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. Remove and cool.

11.6.3 Add an additional 3 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 20 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool.

11.6.4 Add 10 mL of reagent water, cover, and return to the hotplate for 15 minutes. Remove and cool.

11.6.5 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.6.6 The samples are ready for analysis by GFAAS.

11.7 DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS OF As AND Se ONLY BY GFAA (AS)

NOTE: This digestion is applicable only for analysis of arsenic (As) and selenium (Se) by GFAAS.

11.7.1 Add 1 mL of concentrated HNO_3 , 2 mL of 30% hydrogen peroxide, and several boiling chips to each sample, cover with watch glasses, and mix.

11.7.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 50 mL. Remove and cool.

11.7.3 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.7.4 The samples are ready for analysis by GFAAS (for As and Se).

11.8 HOTPLATE DIGESTION OF NON-AQUEOUS AND MULTI-PHASE LIQUIDS FOR ANALYSIS BY ICP, GFAA, OR FLAA (NA) - METHOD 3010M

NOTE: Metal analytes for which this digestion is applicable include:

Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Sb, Se, Na, Ti, V, and Zn.

- 11.8.1 Add 5 mL of concentrated HNO_3 , and several boiling chips to each sample, cover with watch glasses, and mix.
- 11.8.2 Place on a hotplate and maintain at 90-95°C for 15 minutes, or until the volume has been reduced to approximately 10 mL. Remove and cool.
- 11.8.3 Add an additional 5 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool. Add an additional 5 mL of concentrated HNO_3 , cover, and heat for another 30 minutes. Allow the volume to reduce to 5-10 mL. Remove and cool.
- 11.8.4 Add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each sample, cover, and return to the hotplate for 15 minutes. Remove and cool.
- 11.8.5 Rinse down the watchglass and sides of the beakers. Filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:
 - GLA Sample I.D.
 - Matrix type
 - Date digested
 - Dilution factor (where applicable)
- 11.8.6 The samples are ready for analysis by ICP/GFAA/FLAA.

11.9 HOTPLATE DIGESTION OF AQUEOUS AND NON-AQUEOUS LIQUIDS FOR ANALYSIS OF TOTAL RECOVERABLE METALS BY ICP, GFAA, OR FLAA (A)

NOTE: Metal analytes for which this digestion is applicable include:

Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Sb, Se, Na, Ti, V, and Zn.

- 11.9.1 Add 2 mL of concentrated HNO_3 , 5 mL of concentrated HCl , and several boiling chips to each sample, cover with watch glasses, and mix.
- 11.9.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. **Do not boil samples!** Remove and cool.
- 11.9.3 Rinse down the watchglass and sides of the beakers. Filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:
 - GLA Sample I.D.
 - Matrix type
 - Date digested
 - Dilution factor (where applicable)
- 11.9.4 The samples are ready for analysis by ICP/GFAA/FLAA.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

13.0 REFERENCES

- 13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
- 13.2 EPA Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry
- 13.3 Method 3030: Preliminary Treatment of Samples, Sections E (Nitric Acid Digestion), F (Nitric Acid-Hydrochloric Acid Digestion), and K (Microwave-Assisted Digestion); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
- 13.4 Method SW-846, 3050B: Acid Digestion of Sediments, Sludges, and Soils.
- 13.5 Great Lakes Analytical Quality Assurance Program.
- 13.6 Great Lakes Analytical Chemical Hygiene Plan.
- 13.7 Great Lakes Analytical SOP for Login Department.
- 13.8 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

See References.

APPENDIX A.

METHOD EXCEPTIONS.

A.1 Section 1.0 - Sample Preservation

EPA 200 Series, section 4.1.4:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

SM-3030-F:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

A.2 Section 11.5 (ICP)

EPA Method 200.7:

- Section 11.2.3 - Acid concentrations are made in accordance with SW-846 3010A. The higher concentrations of acid will not compromise the digestion process.
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-F:

- Additions of acid are made in accordance with SW-846 3010B. The higher concentrations of acid will not compromise the digestion process.

A.3 Section 11.6 (GF)

EPA Method 200.9:

- Section 11.3.3 -The addition of hydrochloric acid in step 11.3.3 has been omitted, and an additional additions of nitric acid are made in its place. The interferences associated with chloride in graphite furnace analysis are well documented (for example, in EPA 200 Series, section 4.1.3).
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-E:

- Additions of acid are made in accordance with SW-846 3010B. The higher concentrations of acid will not compromise the digestion process.

A.4 Section 11.7 (AS)

SW-846 Methods 7060A and 7740A:

- The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

EPA 200 Series, Methods 206.2 and 270.2:

- The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

A.5 Section 11.8 (NA)

Modified SW-846 Method 3010A (GLA Method 3010M):

- This method parallels SW-846 Method 3010A. The addition of hydrochloric acid has been replaced by addition of 3 mL of nitric acid. This method is used exclusively for the digestion of gasoline, diesel, oil, and oil sludge waste samples, and aqueous samples with a high organic content. These materials show a wide variance of analyte levels and these digestates are analyzed by ICP, GFAAS, or FLAA.
- For non-aqueous or multi-phase samples, a 5-25 g sample is taken, depending upon organic content and allowable regulatory detection levels required. This dilution factor is included in the final calculations of analyte concentrations.

APPENDIX B.
STANDARD SPIKING LEVELS AND VOLUMES.

Standard	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume
GLA-SPK-1A		0.05/50	0.10/50	0.10/50
GLA-SPK-3B	0.05/50		0.10/50	0.10/50
GLA-SPK-4B				
GLA-SPK-5		0.05/50	0.10/50	0.10/50
GLA-SPK-6				0.10/50
EARTH		0.10/50	0.10/50	

Corresponding Elements and Concentrations (mg/L) per Matrix

Set	Element	D H ₂ O FNC	D H ₂ O ICP	H ₂ O	TCLP/SPLP Ext.
R C R A	Ag	0.005		0.01	0.51
	As	0.015		0.03	0.03
	Ba		0.50	1.0	1.0
	Cd	0.001		0.002	0.502
	Cr	0.003	0.50	1.006	1.006
	Hg	0.001		0.002	0.002
	Pb	0.015		0.03	0.03
	Se	0.015		0.03	0.03

P R I R T Y	Be		0.50	1.0	1.0
	Cu	0.015	0.50	1.03	1.03
	Ni		0.50	1.0	1.0
	Sb	0.015	1.0	2.03	2.03
	Tl	0.015	1.0	2.03	2.03
	Zn		0.50	1.0	1.0

T A L	Al		0.5	1.0	1.0
	Co		0.5	1.0	1.0
	Fe		0.5	1.0	1.0
	Mn		0.5	1.0	1.0
	V		0.5	1.0	1.0

E A R T H	Ca		1.0	1.0	
	K		1.0	1.0	
	Li		1.0	1.0	
	Na		1.0	1.0	
	Mg		1.0	1.0	

E X T R A	B		1.0	2.0	2.0
	Mo		1.0	2.0	2.0
	Si		1.0	2.0	2.0
	Sn		1.0	2.0	2.0
	Ti		1.0	2.0	2.0

APPENDIX B (cont.)

Spiking standard stock solutions :

GLA-SPK-1A

Sb, B, Mo, Si, Sn, Ti	1000 mg/L
-----------------------	-----------

GLA-SPK-3B

Sb, As, Cu, Pb, Se, Ti	15 mg/L
Ag	5 mg/L
Cr	3 mg/L
Cd, Hg	1 mg/L

GLA-SPK-4B

Ti	2000 mg/L
Al, Ba, Be, Cd, Cr, Co, Cu,	1000 mg/L
Fe, Pb, Mn, Ni, Ag, V, Zn	1000 mg/L
As, Se	30 mg/L

GLA-SPK-5

Ti	1000 mg/L
Al, Ba, Be, Cr, Co, Cu,	500 mg/L
Fe, Mn, Ni, v, Zn	500 mg/L

GLA-SPK-6

Cd, Ag	250 mg/L
--------	----------

CLPP-ICS-A

Al, Ca, Mg	5000 mg/L
Fe	2000 mg/L

EARTH METALS

Ca, Mg, K, Na	10000 mg/L
---------------	------------

APPENDIX C.

METALS GLASSWARE PREPARATION

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.
2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.
3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.
4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.



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STANDARD OPERATING PROCEDURE (018) METHOD CLARIFICATION

Date Effective: 12/1/98 Supersedes: 10/1/93

Method No.: EPA 200.7 Method Title: Liquid extractions for FLAA / ICP

The above method is currently being used with the following clarificationstions:

Liquid extractions for ICP and FLAA are being compiled into one extraction called EPA 200.7. This was done as a time saving measure for sample preparation. Two milliliters of concentrated HNO₃ and five milliliters of concentrated HCL are added to each 100 ml of sample. Each sample is then gently heated, not boiled until a volume of approximately 20 ml has been reached. Ribbed watch glass are used during this process. Afterwards, each sample is allowed to cool and is then filtered to a final volume of 100 ml with deionized water. This method takes the place of EPA Methods 200.7, 3005, and 3010.

The following have been added to the analyte list:

Germanium
Tantalum

CAS No.: 7440-56-4
CAS No.: 7440-25-7

Approved: 

Date: 2-1-98

NOTE: The above information reflects current modifications to the method. Please reference the specific section modified through the numerical designation used by the procedure and give a brief explanation why the modification has been made.

TITLE: Acid Digestion Of Aqueous Samples And Extracts For Total Metals
For Analysis By FLAA Or ICP Spectroscopy

1.0 SCOPE AND APPLICATION

- 1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FL M) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.
- 1.2 Samples prepared by Method 3010A may be analyzed by FLAA or ICP for the following:

ANALYTE:	CAS #
Aluminum	7429-90-5
Al	
Arsenic (*)	7440-38-2
As	
Barium	7440-39-3
Ba	
Beryllium	7440-41-7
Be	
Cadmium	7440-43-9
Cd	
Calcium	7440-70-2
Ca	
Chromium	7440-47-3
Cr	
Cobalt	7440-48-4
Co	
Copper	7440-50-8
Cu	
Iron	7439-89-6
Fe	
Lead	7439-92-1
Pb	
Magnesium	7439-95-4
Mg	
Manganese	7439-96-5
Mn	
Molybdenum	7439-98-7
Mo	
Nickel	7440-02-0
Ni	
Potassium	7440-09-7
K	
Selenium (*)	7782-49-2

Se	
Sodium	7440-23-5
Na	
Thallium	7440-28-0
Tl	
Vanadium	7440-62-2
V	
Zinc	7440-66-6
Zn	

(*) Analysis by ICP

INSTRUMENTATION: N/A

NOTE: See Method 7760 for the digestion and FLAA analysis of Silver.

1.3 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization. Consult Method 3020A for samples requiring graphite furnace analysis.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

- 4.1 Griffin beakers - 150-mL or equivalent.
- 4.2 Watch glasses - Ribbed and plain or equivalent.
- 4.3 Qualitative filter paper or centrifugation equipment.
- 4.4 Graduated cylinder or equivalent - 100mL.
- 4.5 Funnel or equivalent.
- 4.6 Hot plate or equivalent heating source - adjustable and capable of maintaining a temperature of 90-95-C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the

specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

- 5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.
- 5.3 Nitric acid (concentrated), HNO_3 . Acid should be analyzed to determine levels of impurities. If method blank is $< \text{MDL}$, the acid can be used.
- 5.4 Hydrochloric acid (1:1), HCl . Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is $< \text{MDL}$, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.
- 6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.
- 6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3 .

7.0 PROCEDURE

- 7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3 . Cover the beaker with a ribbed watch glass or equivalent. Place the beaker on a hot plate or equivalent heating source and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3 . Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

[NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.]

- 7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.
- 7.3 Wash down the beaker walls and watch glass with water and, when

necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned. Rinse the filter and filter apparatus with dilute nitric acid and discard the rinsate. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%. The sample is now ready for analysis.

8.0 QUALITY CONTROL

- 8.1 All quality control measures described in Chapter One should be followed.
- 8.2 For each analytical batch of samples processed, blanks (calibration and reagent) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for proper protocol when analyzing blanks.
- 8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Refer to Chapter One for proper protocol when analyzing replicates.
- 8.4 Spiked samples or standard reference materials should be employed to determine accuracy. Refer to Chapter One for proper protocol when analyzing spikes.
- 8.5 The method of standard addition shall be used for the analysis of all EP extracts and delisting petitions (see Method 7000A, Step 8.7). Although not required, use of the method of standard addition is recommended for any sample that is suspected of having an interference.

9.0 METHOD PERFORMANCE

- 9.1 No data provided.

10.0 REFERENCES

- 1. Rohrbough, W.G.; et al. Reagent Chemicals. American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
- 2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DIGESTION OF SOLIDS FOR THE ANALYSIS OF METALS

GLA 3050 BG

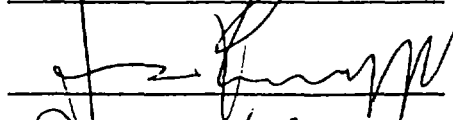
Revision 3.1

Approved By:

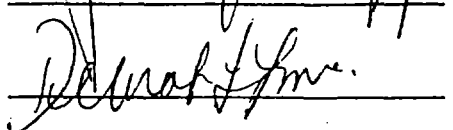
Department Manager:

 Date: 5/27/99

Quality Assurance Manager:

 Date: 5/27/99

Laboratory Director:

 Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the sample handling and digestion of solids in preparation for analysis of total metals by ICP-OES and FLAA/GFAAS. This SOP is an interpretation of EPA Methods 300.7 and 300.9; Standard Methods no. 3030, Sections E, F, and K; and SW-846 no. 3050B. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

NOTE: The digests produced using this procedure are not suitable for the analysis of mercury (Hg) or hexavalent chromium (Cr^{6+}).

1.1 MATRICES

This method is applicable to soils, solids (such as wipes and paints), sediments, and sludges. This method is a very strong acid digestion that will dissolve almost all elements; however, silicate structures are not normally dissolved.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

A representative portion of sample is digested with nitric acid and hydrogen peroxide, and then refluxed with additional nitric (for SW-846 method 3050B) or nitric/hydrochloric acids (EPA method 200.7). The digestate is then filtered and diluted for analysis by ICP, GFAAS, and/or FLAA. A separate sample is dried if necessary for dry weight calculations. Solid matrix types and amounts used include:

- Soils and sediments - 1-2 g portion.
- Paint chips - up to 2 g.
- Paint or dust wipes and filters - entire wipe or filter (including washings).
- Waste sludges - a larger portion may be taken based upon the dry weight, up to 2 g of solid.
- Miscellaneous - mixed solids, waste oil sludges (may require particle size reduction and sub-sampling).

The approximate linear upper ranges for a 2-g sample size are:

- As, Be, Cd, Co, Cr, Cu, Mo, Ni, Se, Ti, V, Zn - 1,000,000 mg/kg.
- Pb, Sb - 200,000 mg/kg.
- Ag, Ba - 2500 mg/kg.

Smaller sample sizes should be taken if limits are exceeded.

See Appendix A for method exceptions.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 CHEMICALS SPECIFIC TO DIGESTIONS

30% Hydrogen peroxide is a strong oxidizer in the presence of acids, and can cause burns to eyes and skin. It can react violently when introduced to a sample in concentrated acid. Large volumes of hydrogen gas may be produced. Allow samples to cool thoroughly before adding hydrogen peroxide. Similarly, add concentrated nitric acid to samples carefully.

4.0 INTERFERENCES

- 4.1 Sample matrices can vary greatly, even within specific sample type groups, most notably waste sludges (for example, soil versus water treatment waste sludge). Any sample types exhibiting significantly different properties, such as high organic content or multi-phase samples, are to be handled as individual matrices, and appropriate matrix spikes should be produced and analyzed.
- 4.2 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed following the procedure outlined in Appendix C. Periodic cleaning of sample preparation and analysis areas, will be performed.

5.0 RECORD KEEPING

- 5.1 Each analyst is responsible for keeping accurate and up-to-date records of all digestions performed.
- 5.2 Digestion Log Book:

A log book will be maintained for all solid matrix types and associated digestions. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample weight used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Reviewer's signature and date
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final digestate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

- 5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (e.g. a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedures for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

8.3 METHOD DETECTION LIMIT STUDY

- 8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:
- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
 - Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's *t* value at *n*-1 degrees of freedom (3.143 for seven replicates).
- 8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.
- 8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

- 9.1 Beakers, Griffin type, 250-mL size.
- 9.2 Watch covers, ribbed, 90-mm diameter.
- 9.3 Volumetric flasks, 25-100 mL (wide mouth).
- 9.4 Glass funnels.
- 9.5 Filter paper - 9 and 15 cm, Whatman 41, or equivalent.
- 9.6 Sample containers, 50 or 100-mL capacity, metal-free.
- 9.7 Hotplate, adjustable, capable of maintaining a constant temperature for samples of 90-95°C. Monitor temperature of the hotplate by placing an Erlenmeyer flask with approximately 100 mL of cooking oil at the center of the hotplate, and reading the temperature with an ASTM thermometer positioned with the bulb against the bottom of the flask. The temperature must be at least 140°C. Record temperatures in the log book.
- 9.8 Analytical balance, calibrated - capable of weighing to nearest 0.1 g for soil/sediment/sludge samples, 0.001 g for paints.
- 9.9 Hot block digestion apparatus:
- HotBlock, Environmental Systems, set to maintain a sample temperature of 90-95°C.
 - Polyolefin digestion vessels, 50-mL size, with watch covers and snap-on caps.

10.0 STANDARDS AND REAGENTS

- 10.1 Reagent water - ASTM Type II Water (DI water).
- 10.2 Nitric acid - concentrated HNO₃, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
- 10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
- 10.4 Hydrogen peroxide - 30% H₂O₂, ACS/analytical reagent grade, Fisher no. H325. **CAUTION:** Hydrogen peroxide is an oxidizer.
- 10.5 Spiking standards - GLA-SPK-1A and -4B, Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. (Refer to Appendix B for concentrations and volumes spiked.)

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 SELECTION OF DIGESTION PROCEDURE

The appropriate method for the required metal analysis must be referenced in order to select the proper digestion procedure. There are several methods for digestions which can be selected based upon the matrix type of the sample and the type of digestion being performed. Use Table 1 to determine which method is most applicable to the samples being analyzed. The proper digestion procedure is selected from Table 2.

Table 1. Digestion Method Reference Chart.					
Analysis	Method Reference	Microwave Digestions	Standard Digestions		
			ICP/FLAA	GFAA	Special
Total Metals	SW-846	3051A	3050B + HCl	3050B + HNO ₃	7060A (As) 7740A (Se)
	EPA	n/a	200.7	200.9	206.2 (As) 270.2 (Se)
Air Filters	NIOSH	n/a	7082	7082	n/a

Table 2. Procedure Selection Table.				
Digestion Type	Analysis Type	Analysis Method	Applicable Method(s)	Digestion Procedure
Standard	Total Metals	Any (1)	SW-846 3050B EPA 200.9 (3)	11.4 (GEN)
Standard	Air Filter - Lead Only	Any (1)	NIOSH 7082	11.4 (GEN)
Standard	Total Metals (2)	ICP/FLAA	SW-846 3050B EPA 200.7 (4)	11.5 (ICP)
HotBlock	Total Metals	Any (1)	SW-846 3050B	11.6 (HB)
(1) Any analytical method refers to GLA routine methods : ICP, GFAAS, and FLAA. These digests are not suitable for analysis of mercury or hexavalent chromium. (2) For samples requiring addition of hydrochloric acid. This procedure produces digestates which can only be analyzed by ICP-OES. (3) Samples are refluxed with nitric acid for metals determination by all analytical methods. (4) Samples are refluxed with hydrochloric acid for metals determination by ICP-OES only.				

11.2 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) **before beginning the analysis**.

CAUTION: All hotplate digestions must be performed in a fume hood.

11.3 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.3.1 Soil, sediment, and other solid samples:

- Samples - A representative 2.0g +/- 0.01g (1.0 g for hotblock digestion, section 11.6) aliquot is weighed into a clean beaker (or digestion tube for hotblock digestion).
- Matrix spikes - Measure two additional aliquots of one sample, with weights similar to the test sample weight, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.1 mL each of GLA-SPK-1A, -4B, As/Se Soln., and -EM into the sample replicates, and mark them as MS and MSD.
- LCS - Combine 7.5ml of reagent water and 7.5ml of nitric acid. Accurately aliquot 0.05ml each of GLA-SPK-1A, -4B, As/Se Soln., and -EM into the solution, and mark the sample as LCS.

Note: If requested, the sample weight can be based on dry-weight –corrected soil. Refer to SOP GLA160BG for instructions on determining dry weight.

11.3.2 Sludge/high water content samples:

- Samples - Each sample should be well mixed before taking a representative portion for digestion. If the sample contains significant water, upon client request, a dry weight determination may be performed prior to digestion (See SOP GLA160BG for dry weight determination), and the sample size adjusted and/or calculated as follows:

$$\text{sample weight (g)} = \frac{2.0 \text{ (1.0 for hotblock) g}}{\text{dry weight (as decimal percent)}}$$

- Matrix spikes - Measure two additional aliquots of one sample, with weights similar to the test sample weight, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.1 mL each of GLA-SPK-1A, -4B, As/Se Soln., and -EM into the sample replicates. Add 5 mL of reagent water to each, washing the spike solutions into the beakers or vessels. Mark as MS and MSD.
- LCS - Combine 7.5ml of reagent water and 7.5ml of nitric acid. Accurately aliquot 0.05ml each of GLA-SPK-1A, -4B, As/Se Soln., and -EM into the solution, and mark the sample as LCS.

11.3.3 Wipes samples (surrogate matrix QC):

- Samples - Transfer the entire wipe into a clean beaker along with any liquid and/or loose material which has fallen off the wipe. Rinse the sample container with three successive portions of reagent water, adding each rinsate to the beaker.
- Surrogate matrix blank - Place a 9- or 15-cm Whatman 41 filter paper into a clean beaker. Add 15 mL of reagent water.
- LCS - Place 9- or 15-cm Whatman 41 filter paper into two clean and dry beakers. Weigh 0.02-0.04 g of NIST SRM1579a onto the filter paper. Allow any paint dust from the SRM addition to settle, and record an accurate weight in the log book to the nearest 0.0001 g. Carefully add 15 mL of reagent water.

11.3.4 Paint/paint dust samples:

- Samples - Weigh as large a portion as possible, up to 2 g (accurately to the nearest 0.0001 g), into a clean beaker. Record the weight(s) in the log book.
- Surrogate matrix spike samples - Place 9 (or 15) cm Whatman 41 filter paper into two clean and dry beakers. Weigh 0.02-0.04 g of NIST SRM1579a onto the filter paper. Allow any paint dust from the SRM addition to settle, and record an accurate weight in the log book to the nearest 0.0001 g. Carefully add 15 mL of reagent water.

11.4 HOTPLATE DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES, GFAAS, OR FLAA (GEN)

NOTE: Metal analytes for which this digestion is applicable include:

Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Ti, V, Zn.

- 11.4.1 Add 5 mL of reagent water (except for wipes samples), 5 mL of concentrated HNO_3 , and several boiling chips to each sample, cover with watchglasses, and mix.
- 11.4.2 Place on a hotplate and maintain at 90-95°C for 15 minutes. Remove and cool.
- 11.4.3 Add an additional 5 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Remove and cool.
- 11.4.4 Add a third 5 mL portion of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Allow solutions to evaporate to approximately 5 mL. Remove and cool.
- 11.4.5 After the samples have cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each. Warm gently if necessary to start the peroxide reaction. Heat until the effervescence subsides. Make further 1 mL additions of hydrogen peroxide until the effervescence is minimal, or the general sample appearance remains unchanged. Return to the hot plate for 15 minutes to destroy excess peroxide.
- 11.4.6 Transfer the digestate to a 100-mL volumetric flask. Dilute to the mark with reagent water and mix. If samples are to be analyzed immediately, filter the digestate through a Whatman 41 filter paper into a metal-free container. Otherwise, samples may be allowed to settle 1 hour, or overnight, prior to analysis. The container should be labeled with:
 - GLA Sample I.D.
 - Matrix type
 - Date digested
 - Dilution factor, if other than standard weight or volume (where applicable)
- 11.4.7 The samples are ready for analysis by ICP, GFAAS, or FLAA.

11.5 HOTPLATE DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES OR FLAA ONLY (ICP)

NOTE: Metal analytes for which this digestion is applicable include:

Al, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Ti, V, and Zn.

- 11.5.1 Add 5 mL of reagent water (except for wipes samples), 5 mL of concentrated HNO_3 , and several boiling chips to each sample, cover with watch glasses, and mix.
- 11.5.2 Place on a hotplate and maintain at 90-95°C for 15 minutes. Remove and cool.
- 11.5.3 Add an additional 5 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Remove and cool.
- 11.5.4 Add a third 5 mL portion of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Allow solutions to evaporate to approximately 5 mL. Remove and cool.
- 11.5.5 After the samples have cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each. Warm gently if necessary to start the peroxide reaction. Heat until the effervescence subsides. Make further 1 mL additions of hydrogen peroxide until the effervescence is minimal, or the general sample appearance remains unchanged. Return to the hot plate for 15 minutes to destroy excess peroxide.

- 11.5.6 Add 5 mL of concentrated HCl and 10 mL of reagent water to each sample. Cover and return to hotplate for 15 minutes. Remove and cool.
- 11.5.7 Transfer the digestate to a 100-mL volumetric flask. Dilute to the mark with reagent water and mix. Filter the digestate through a Whatman 41 filter paper into a metal-free container. The container should be labeled with:
- GLA Sample I.D.
 - Matrix type
 - Date digested
 - Dilution factor, if other than standard weight or volume (where applicable)
- 11.5.8 The samples are ready for analysis by ICP or FLAA.

11.6 HOTBLOCK DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES, GFAAS, OR FLAA (HB)

NOTE: Metal analytes for which this digestion is applicable include:

Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Ti, V, Zn.

NOTE: This procedure is not applicable for wipes samples.

- 11.6.1 Add 5 mL of reagent water (except for wipes samples) and 7.5 mL of concentrated HNO₃ to each sample. Cover and mix.
- 11.6.2 Place in digester and heat for 75 minutes, maintaining sample temperatures of 95-100°C. Remove and cool.
- 11.6.3 After the samples have cooled, slowly and carefully add 1 mL of 30% hydrogen peroxide to each. Allow vigorous reaction to subside. Place in digester and heat for 15 minutes, maintaining sample temperatures of 95-100°C. Remove and cool.
- 11.6.4 Bring total sample volumes to 50 mL each with reagent water, cover and mix. Allow samples to settle at least 1 hour (or overnight). If immediate analysis is required, samples may be filtered through Whatman 41 filter paper. The container should be labeled with:
- GLA Sample I.D.
 - Matrix type
 - Date digested
 - Dilution factor (where applicable)
- 11.6.5 The samples are ready for analysis by ICP, GFAAS, or FLAA.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

13.0 REFERENCES

- 13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
- 13.2 EPA Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry.
- 13.3 Method 3030: Preliminary Treatment of Samples, Sections E (Nitric Acid Digestion), F (Nitric Acid-Hydrochloric Acid Digestion), and K (Microwave-Assisted Digestion); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
- 13.4 Method SW-846, 3050B: Acid Digestion of Sediments, Sludges, and Soils.
- 13.5 NIOSH Method 7082: Analysis of Lead in Air Filters.
- 13.6 Great Lakes Analytical Quality Assurance Program.
- 13.7 Great Lakes Analytical Chemical Hygiene Plan.
- 13.8 Great Lakes Analytical SOP for Login Department.
- 13.9 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to the Great Lakes Analytical Quality Assurance Program Manual.

APPENDIX A.

METHOD EXCEPTIONS.

A.1 Section 1.0 - Sample Preservation

EPA 200 Series, section 4.1.4:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

SM-3030-F:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

A.2 Section 11.4 - Sample Digestion (GEN)

EPA Method 200.7:

- Section 11.2.3 - Acid concentrations are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-F:

- Additions of acid are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.

A.3 Section 11.5 - Sample Digestion (ICP)

EPA Method 200.9:

- Section 11.3.3 - The addition of hydrochloric acid has been omitted an additional addition of nitric acid made its place. The interferences associated with chloride in the graphite furnace analysis are well documented in many reference documents (for example, EPA 200 Series, section 4.1.3).
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-E:

- Additions of acid are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.

APPENDIX B.**STANDARD SPIKING LEVELS AND VOLUMES.**

Standard	Aliquot/Volume
GLA-SPK-1A	0.10/100
GLA-SPK-4B	0.10/100
As/Se	0.05/50
EARTH	0.05/100

Corresponding Elements and Concentrations (mg/Kg)

Set	Element	Soil/Solid
R C R A	Ag	1.0
	As	0.53
	Ba	1.0
	Cd	1.0
	Cr	1.0
	Hg	
	Pb	1.0
	Se	0.28

P R I R T Y	Be	1.0
	Cu	1.0
	Ni	1.0
	Sb	1.0
	Tl	2.0
	Zn	1.0

T A L	Al	1.0
	Co	1.0
	Fe	1.0
	Mn	1.0
	V	1.0

E A R T H	Ca	1.0
	K	1.0
	Li	1.0
	Na	1.0
	Mg	1.0

E X T R A	B	1.0
	Mo	1.0
	Si	1.0
	Sn	1.0
	Ti	1.0

APPENDIX B (cont.)

Spiking standard stock solutions :

GLA-SPK-1A

Sb, B, Mo, Si, Sn, Ti	1000 mg/L
-----------------------	-----------

GLA-SPK-4B

Ti	2000 mg/L
Al, Ba, Be, Cd, Cr, Co, Cu,	1000 mg/L
Fe, Pb, Mn, Ni, Ag, V, Zn	1000 mg/L
As, Se	30 mg/L

EARTH METALS

Ca, Mg, K, Na	10000 mg/L
---------------	------------

As/Se Solution

As, Se	1000 mg/L
--------	-----------

APPENDIX C.

METALS GLASSWARE PREPARATION

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.
2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.
3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.
4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water Immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.



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STANDARD OPERATING PROCEDURE (018a) METHOD CLARIFICATION

Date Effective: 12/1/98 Supersedes: 9/1/91

Method No.: EPA 3050A Method Title: Solids extractions for FLAA / ICP

The above method is currently being used with the following clarificationstions:

The top one inch in eaach soil tube is discarded and a small amount of sample is mixed since multiple analyses would be required using the same soil cores, including volatile organic tests. To get better homogeneity, soil cores would have to be taken for inorganic analyses separately from those for volatile organics.

The following have been added to the analyte list:

Germanium
Tantalum

CAS No.: 7440-56-4
CAS No.: 7440-25-7

Approved: _____

Date: 12-1-98

NOTE: The above information reflects current modifications to the method. Please reference the specific section modified through the numerical designation used by the procedure and give a brief explanation why the modification has been made.

TITLE: Acid Digestion Of Sediments, Sludges, And Soils

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Step 2.1):

ANALYTE:	CAS #
FLAA	
Aluminum	7440-36-0
Al	
Barium	7440-39-3
Ba	
Beryllium	7440-41-7
Be	
Cadmium	7440-43-9
Cd	
Calcium	7440-70-2
Ca	
Chromium	7440-43-9
Cr	
Cobalt	7440-48-4
Co	
Copper	7440-50-8
Cu	
Iron	7439-89-6
Fe	
Lead	7439-92-1
Pb	
Magnesium	7439-95-4
Mg	
Manganese	7439-96-5
Mn	
Molybdenum	7439-98-7
Mo	
Nickel	7440-02-0
Ni	
Osmium	7440-04-2
Os	
Potassium	7440-09-7
K	
Silver	7440-22-4

Ag	
Sodium	7440-23-5
Na	
Thallium	7440-28-0
Tl	
Vanadium	7440-62-2
V	
Zinc	7440-66-6
Zn	

GFAA

Arsenic	7440-38-2
As	
Beryllium	7440-41-7
Be	
Cadmium	7440-43-9
Cd	
Chromium	7440-43-9
Cr	
Cobalt	7440-48-4
Co	
Iron	7439-89-6
Fe	
Lead	7439-92-1
Pb	
Molybdenum	7439-98-7
Mo	
Selenium	7782-49-2
Se	
Thallium	7440-28-0
Tl	
Vanadium	7440-62-2
V	

[NOTE See Method 7760 for FLAA preparation for Silver.]

INSTRUMENTATION: N/A

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used for flame AA and ICP analyses and nitric acid is used for furnace AA work. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, Tl,

and V. The diluted samples have an approximate acid concentration of 5.0% (v/v). A separate sample shall be dried for a total % solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

- 4.1 Conical Phillips beakers - 250-mL, or equivalent.
- 4.2 Watch glasses ribbed or equivalent.
- 4.3 Drying ovens - That can be maintained at 30°C.
- 4.4 Thermometer - That covers range of 0-200-C.
- 4.5 Filter paper - Whatman No. 41 or equivalent.
- 4.6 Centrifuge and centrifuge tubes.
- 4.7 Analytical Balance - Capable of accurately weighing to the nearest 0.01 g.
- 4.8 Electric Hot Plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95-C.
- 4.9 Glass Funnel or equivalent.
- 4.10 Graduated cylinder or equivalent.

5.0 REAGENTS

- 5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.
- 5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.
- 5.3 Nitric acid (concentrated), HNO_3 . Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.
- 5.4 Hydrochloric acid (concentrated), HCl . Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.
- 5.4 Hydrogen peroxide (30%), H_2O_2 . Oxidant should be analyzed to determine level of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.
- 6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.
- 6.3 Nonaqueous samples shall be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

- 7.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker 1.00-2.00 g of sample. For samples with low percent solids a larger sample size may be used as long as digestion is completed.
- 7.2 Add 10 mL of 1:1 HNO₃, mix the slurry, and cover with a watch glass. Heat the sample to 95-C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO₃, replace the watch glass, and reflux for 30 minutes. Repeat this last step to ensure complete oxidation. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.
- 7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H₂O₂. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.
- 7.4 Continue to add 30% H₂O₂ in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

[NOTE: Do not add more than a total of 10 mL 30% H₂O₂.]

- 7.5 If the sample is being prepared for (a) the ICP analysis of As and Se, or (b) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of water, return the covered beaker to the hot plate, and reflux for an additional 15 minutes without boiling. After cooling, dilute to a 100 mL volume with water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.5.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO₃. The sample is now ready for

analysis.

- 7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Co, Cr, Fe, Mo, Pb, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.6.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO₃. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.7 Calculations

7.7.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.7.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, preparation blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials must be employed to determine accuracy. A spiked sample should be included with each batch of samples processed and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.
3. Edgell, K.; USEPA Method Study 37 - SW-846 Method 3050 Acid Digestion of Sediments, Sludges, and Soils. EPA Contract No. 68-03-3254, November 1988.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

ORGANIC EXTRACTION AND SAMPLE PREPARATION FOR

SEMIVOLATILE DETERMINATIVE METHODS

GLA 3500 BG

Revision 1.1

Approved By:

Department Manager:

Alecia Bazz

Date: 5-28-99

Quality Assurance Manager:

[Signature]

Date: 5/28/99

Laboratory Director:

Danab Love

Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the selection and use of procedures for the extraction, dilution, and cleanup of samples for analysis by semivolatile determinative methods. This SOP is an interpretation of several EPA extraction methods, including 3500B, 3510C, 3550B, and 3580A, and cleanup methods 3620B, 3640A, 3660B, and 3665A. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for aqueous, soil/sediment, solid waste, and non-aqueous solvent-soluble waste samples.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

- 2.1 Samples of known volume or weight are extracted with solvent, or diluted with solvent, in preparation for analysis. One of the following methods is used depending upon sample type:
- Aqueous samples are extracted using separatory funnel liquid-liquid extraction (method 3510C). For example, 1000 mL of sample is extracted using three 60 mL portions of methylene chloride (section 11.1).
 - Soil/sediment samples are extracted using ultrasonic extraction (method 3550B). For example, 30 g of sample is extracted using three 100 mL portions of methylene chloride (sections 11.3 and 11.4).
 - Samples for herbicide analysis are extracted and derivatized using diazomethane (method 8151, sections 11.2 and 11.5).
 - Non-aqueous solvent soluble samples are diluted (method 3580A). For example, 1-2 g of sample is mixed with 10 mL of methylene chloride (section 11.6).
- 2.2 Some samples may be required to be placed through a cleanup procedure to eliminate interferences. Sample cleanup procedures are:
- Samples for PCB analysis are treated with sulfuric acid (method 3665A) to remove interferences (section 12.1). Sulfur cleanup is required following the sulfuric acid cleanup procedure.
 - Soluble sulfur can be removed using copper (method 3660B, section 12.2).
 - Florisil (magnesium silicate) may be used to separate analytes from interfering compounds (method 3620B, section 12.3).
 - Cleanup using gel permeation chromatography (GPC, method 3640A) may be used to separate molecules of different sizes (section 12.4)
- 2.3 The resultant extracts are dried using anhydrous sodium sulfate and concentrated using Kuderna-Danish (K-D) apparatus, or in an automated concentration device. The extracts are analyzed, for example, per one of EPA methods 8015, 8081, 8082, 8151, 8270, or 8310.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents (use nitrile gloves to avoid contamination with plasticizers).

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples (use nitrile gloves to avoid contamination with plasticizers). Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials are demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Soap residue (for example, sodium dodecyl sulfate), which causes a basic pH on glassware surfaces, may cause degradation of certain analytes. In general, glassware is washed using Contrad or Alconox detergent, and then rinsed thoroughly with organic-free deionized water, acetone, and finally with methylene chloride.

4.2 Phthalate esters contaminate many types of products found in the laboratory. Plastics, in particular, are not used because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced. Nitrile gloves must be used.

4.3 Materials causing interferences may be coextracted from a sample. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.

5.0 RECORD KEEPING

5.1 Extraction logbooks contain records of analytical batches.

5.2 Analytical batch records must contain the following information:

5.2.1 Sample volume or weight.

5.2.2 Client name or sample number.

- 5.2.3 Great Lakes sample number.
- 5.2.4 Extraction method.
- 5.2.5 Analytical method.
- 5.2.6 Date(s) extracted and concentrated.
- 5.2.7 Lab batch ID number.
- 5.2.8 Extraction or dilution solvent, and lot number.
- 5.2.9 Final solvent (if different), and lot number.
- 5.2.10 Initials of analyst(s).
- 5.2.11 Lab lot ID# of spiking solution(s).
- 5.2.12 Final volume of extract.
- 5.2.13 Any "cleanup" methods used.

An example of a logbook page for an analytical batch record is attached to this SOP (see Attachment 1).

- 5.3 All unused portions of logbook pages must be z'ed out.

6.0 QUALITY CONTROL

- 6.1 For quality control, each water extraction batch contains a method blank (MB), and laboratory control spike (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). An analytical batch contains no more than 20 samples. Deionized water is used for water method blanks and spikes.
- 6.2 Each soil extraction batch (not more than 20 samples) contains a method blank (MB), a lab control spike (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). Clean sand is used for soil method blanks (MB) and blank spikes (LCS). Soil samples selected randomly by the LIMS are used for matrix spikes and matrix spike duplicates. The extractionists can override this if insufficient sample is available, or if chosen sample is extremely dirty.
- 6.3 Surrogate compounds are added to all samples, blanks, and spikes in an analytical batch.
- 6.4 Descriptions of the standards used for spiking and as surrogates are given in the individual analytical method SOPs. For example, method 8151 (Herbicides) uses a spiking standard containing 0.1 to 1.3 mg/mL of herbicide compounds and a surrogate of 100 µg/mL dichlorophenylacetic acid (DCAA or DCPA).

7.0 SAMPLE MANAGEMENT

- 7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.
- 7.2 LIMS extraction batching procedure:
 - 7.2.1 At the LIMS main menu screen, select B (batching), new batch.
 - 7.2.2 At the Queue prompt, type in "EXTR" and press F8.
 - 7.2.3 Highlight the test wanted from the list of available methods and double-click.
 - 7.2.4 Deselect any samples by clicking on the corresponding √ (check mark).
 - 7.2.5 Click on "Build Batch", then "Add QC". Press "Save".
 - 7.2.6 At name prompt, enter initials of extractionist.
 - 7.2.7 When the batch list appears on screen, highlight "Please Select A Printer", press "List" and choose the "SVOC LIMS Printer".
 - 7.2.8 Select "OK" at all prompts.

8.0 METHOD VALIDATION

Each new extractionist will perform a series of extractions to establish the ability to generate acceptable precision and accuracy. For each analytical method:

- 8.1 Four 1000 mL blank water samples (method validation for water analysis), or four 30 g blank sand samples (method validation for soil analysis), are extracted and concentrated, each spiked with 1.0 mL of the QC spiking solution (see method 3500B, Section 8.2.4).
- 8.2 The extracts will be analyzed and the average percent recovery and the standard deviation of the percent recoveries for each component of the spikes will be calculated.
- 8.3 Acceptance criteria are found in the appropriate determinative method.
- 8.4 Documentation of these analyses will be maintained in the employee's training file.

9.0 EQUIPMENT

NOTE: The exact equipment necessary will depend upon the sample matrix, extraction performed, analytical method, and any clean-up(s) required.

- 9.1 Graduated cylinders - 1000-mL, for measuring volume of aqueous samples.
- 9.2 Separatory funnels - 2-L and 125-mL, with PTFE stopcocks and caps.
- 9.3 pH indicator paper - range to cover pH 0 to 13.
- 9.4 Solvent dispensers, for 30 to 100 mL (two 50-mL dispensers may be used for 100 mL).
- 9.5 Squirt bottles for solvents.
- 9.6 Benchtop shaker, for separatory funnels.
- 9.7 Laboratory timer, clock, or wristwatch.
- 9.8 Erlenmeyer flasks - 500 and 125-mL, for collecting sample extracts.
- 9.9 Filter funnels - 75 mm, fluted bowl, short stem.
- 9.10 Filter paper - Whatman No. 41 (or equivalent) to fit filter funnels.
- 9.11 Boiling chips, PTFE (Teflon).
- 9.12 Spatula, stainless steel or PTFE.
- 9.13 Glass Pasteur pipets.
- 9.14 Kuderna-Danish (K-D) apparatus, each consisting of:
 - Concentrator tube - 10 mL, graduated.
 - Evaporator flask - 500 mL.
 - Snyder column - three-ball macro.
 - Clamps - for securing glassware at ground-glass joints.
- 9.15 Water bath - heated, with concentric ring cover, temperature setting on "High" for approximately 95°C.
- 9.16 Oven, capable of maintaining 400-500°C.
- 9.17 Syringes, glass - 2.5 mL, 1.0 mL, and 100 µL.
- 9.18 Syringe filters - 0.2 µm, 13 mm, Acrodisc, Fisher no. SJFG013NS.
- 9.19 Nitrogen blowdown apparatus - Organomation N-EVAP, or equivalent, connected to nitrogen gas source, temperature setting at about "5" for approximately 50°C bath temperature.
- 9.20 Balance - top-loading, capable of accurately weighing to the nearest 0.01 g.
- 9.21 Beaker - 250 mL, for sonicating samples.
- 9.22 Ultrasonic disrupter - with minimum power of 300 watts, equipped with dual ¾" horns, Heat Systems XL, or equivalent.
- 9.23 Sonabox - used to decrease cavitation sound from disrupter.
- 9.24 Ultrasonic water bath - Branson 8210, or equivalent.
- 9.25 Automatic evaporative concentrator - Zymark Turbo Vap II.
- 9.26 Concentrator tubes - Zymark, 200 mL, 1.0 mL tip.
- 9.27 Glass chromatography column, 20 mm diameter, approximately 30 cm length.
- 9.28 HPLC for GPC cleanup, consisting of:
 - Solvent pump - capable of delivering 5 mL/min.
 - Sample injector - with 0.5 mL sample loop.

- ♦ GPC Cleanup columns - Waters Envirogel, 19 × 150 mm and 19 × 300 mm.
- ♦ UV absorbance detector - with mercury lamp for 254 nm.
- ♦ Flow transfer valve - for eluent to waste or collect.
- ♦ Integrator or chart recorder.
- ♦ Solvent supply and waste containers.

10.0 STANDARDS AND REAGENTS

NOTE: The exact standards and reagents necessary will depend upon the sample matrix, extraction performed, analytical method, and any clean-up(s) required.

- 10.1 Reagent water - organic-free deionized (DI water), Fisher no. W5.
- 10.2 Acetone - pesticide grade or equivalent, Fisher no. A929.
- 10.3 Acetonitrile - pesticide grade or equivalent, Fisher no. A21.
- 10.4 Diethyl ether - pesticide grade or equivalent, Fisher no. E197.
- 10.5 Methanol - pesticide grade or equivalent, Fisher no. A453.
- 10.6 Hexane - pesticide grade or equivalent, Fisher no. H303.
- 10.7 Methylene chloride (MeCl_2) - pesticide grade or equivalent, Fisher no. D151.
- 10.8 Acetone/methylene chloride solution (1:1 v/v) - Mix 500 mL of acetone with 500 mL of methylene chloride in a 1-L bottle.
- 10.9 6%, 15%, and 50% Diethyl ether in hexane solution (v/v) - Mix proportionate volumes of diethyl ether and hexane in a 1-L bottle. For example, 60 mL ether and 940 mL hexane for 6%, 150 and 850 for 15%, or 500 and 500 for 50% (v/v) solutions.
- 10.10 Sodium hydroxide - pellets, NF/FCC grade, Fisher no. S320. **CAUTION:** Sodium hydroxide is corrosive.
- 10.11 Sodium hydroxide solution (10 N) - Dissolve 40 g of sodium hydroxide (NaOH) in water and dilute to 100 mL. **CAUTION:** Reaction is exothermic.
- 10.12 Sulfuric acid - concentrated (18 M), ACS grade, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.
- 10.13 50% Sulfuric acid solution (1:1 v/v) - Carefully pour 50 mL of concentrated sulfuric acid into 50 mL of water. **CAUTION:** Reaction is exothermic.
- 10.14 Hydrochloric acid - concentrated, ACS grade or equivalent, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
- 10.15 Sodium sulfate - granular, anhydrous, Fisher no. S415. Purify by heating at 400-500°C for at least 4 hours.
- 10.16 Acidified sodium sulfate for method 8151 - Slurry 100 g of purified sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH. The pH must be less than 4. Store the remaining solid at 130°C.
- 10.17 Sand - washed sea sand, Fisher no. S25. Purify by heating at 400-500°C for at least 4 hours.
- 10.18 Sodium chloride - analytical reagent grade, Mallinckrodt no. 7581.
- 10.19 Copper - granular or powder, copper should be reactive, as evidenced by a bright shiny appearance, JT Baker no. 1720-01.
- 10.20 Florisil - granular, 60-100 mesh, Fisher F100. Prepared by heating at 400-500°C for at least 4 hours.
- 10.21 GPC Calibration Standards - consisting of corn oil, phthalate, methoxychlor, perulene, and sulfur, Vitron Scientific no. CLP-340.
- 10.22 Diazald, N-methyl-N-nitroso-p-toluenesulfonamide - high purity grade, Aldrich no. D2,800-0.
- 10.23 Ethoxyethoxy ethanol (Carbitol, diethylene glycol monoethyl ether), reagent grade, Aldrich no. E455-0.
- 10.24 Potassium hydroxide - pellets, NF/FCC grade, Mallinckrodt no. 6976. **CAUTION:** Sodium hydroxide is caustic.
- 10.25 Potassium hydroxide solution (37% w/v). Dissolve 37 g of potassium hydroxide (KOH) in water and dilute to 100 mL. **CAUTION:** Reaction is exothermic.

- 10.26 Potassium hydroxide solution (12% w/v). Dilute one volume of 37% KOH solution with two volumes of water. For example, dilute 30 mL KOH solution with 60 mL of water.

11.0 EXTRACTION PROCEDURES

Refer to the summary of extraction procedures, Attachment 2 of this SOP.

11.1 SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (METHOD 3510C)

- 11.1.1 Measure 1000 mL of sample using a 1000-mL graduated cylinder and pour into a labeled 2000-mL separatory funnel. If 1000 mL of sample is not available, use all of the sample and record the volume. Also measure and pour 1000 mL portions of organic-free water into separatory funnels for the method blank, blank spike, and blank spike duplicates.

NOTE: If high analyte concentrations are anticipated, a smaller sample volume may be measured and diluted to 1000 mL with water. Record the volume used for later calculations of dilution factor and analyte concentrations.

- 11.1.2 Using a 1.0-mL syringe, add 1.0 mL (50 μ L for 8015 methods) of the appropriate surrogate spiking solution to each sample, blank and QC sample in the analytical batch and mix well. For the blank spike and blank spike duplicate samples, add 1.0 mL of spiking solution to 1000 mL aliquots of blank reagent water.

- 11.1.3 For methods 8081, 8082, and 8270, check the pH of the sample(s) with pH paper. If necessary, adjust the pH using 50% (1:1 v/v) sulfuric acid solution or 10 N sodium hydroxide, to the following pH values:

- Method 8081 - between 5 and 9 (inclusive).
- Method 8082 - between 5 and 9 (inclusive).
- Method 8270 - first set of extractions ≤ 2 , second set of extractions ≥ 11 .

Samples for methods 8015 and 8310 do not require checking or adjustment.

- 11.1.4 For each sample, use 60 mL of methylene chloride (60 mL of hexane for method 8015D) to rinse the sample bottle and the graduated cylinder. Transfer to the separatory funnel. Seal and shake the separatory funnel vigorously for two minutes with periodic venting to release excess pressure.

CAUTION: Organic solvents can create excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel is vented into a hood to avoid exposure of the analyst to solvent vapors.

- 11.1.5 Allow the organic layer (*i.e.* the bottom layer if methylene chloride, top layer if hexane) to separate from the water phase. The layers should be visually separate. Collect the solvent extract in a 500-mL Erlenmeyer flask.

NOTE: If the emulsion interface between layers is more than about 1/3 the size of the solvent layer, additional techniques to complete the phase separation must be employed. The optimum technique depends upon the sample and may include slow draining of the solvent, stirring, filtration of the emulsion through glass wool and/or sodium sulfate, or dissolving sodium chloride in the sample.

- 11.1.6 Repeat the extraction two more times using fresh 60 mL portions of solvent. Combine the three solvent extracts in the Erlenmeyer flask. Combine all extracts in the Erlenmeyer flask.

NOTE: If extracting sample for method 8270, perform three extractions. Then adjust the pH of the sample to ≥ 11 using 10 N sodium hydroxide and re-extract the sample three more times.

11.1.7 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Then pass the extract through a filter funnel, containing a folded filter paper containing some sodium sulfate, into the K-D concentrator. Rinse the Erlenmeyer extract flask with about 20-25 mL of solvent, and pass through the drying funnel into the K-D concentrator. Then rinse the drying funnel with about 15-20 mLs of solvent. Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column.

11.1.8 Place the K-D apparatus on the hot water bath so the concentrator tube is partially immersed in the water. When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

NOTE: If a solvent exchange is required (for example, hexane for methods 8015, 8081, 8082, and acetonitrile for method 8310), do not remove the K-D apparatus, pour 50 mL of hexane, or 10 mL of acetonitrile, into the top of the Snyder column, and concentrate the extract back down to 1-5 mL. Then remove the K-D apparatus from the bath and allow to drain and cool.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

11.1.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. For method 8310, add acetonitrile to a final volume of 10 mL. For methods 8015, 8081, 8082, and 8070, use the nitrogen blowdown apparatus to reduce the extract volume to 1 mL.

11.1.10 If extract requires cleanup, see appropriate cleanup procedure(s), Section 12.0.

11.1.11 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.2 SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION AND DERIVATIZATION FOR HERBICIDES (METHOD 8151)

CAUTION: Notify the Inorganics Department that ether will be in use.

11.2.1 Measure 1000 mL of sample using a 1000-mL graduated cylinder and pour into a labeled 2000-mL separatory funnel. If 1000 mL of sample is not available, use all of the sample and record the volume. Also measure and pour 1000 mL portions of organic-free water into separatory funnels for the method blank, blank spike, and blank spike duplicates.

11.2.2 Using a 1.0-mL syringe, add 1.0 mL of appropriate surrogate spiking solution to each sample, blank and QC sample in the analytical batch and mix well. For the blank spike and blank spike duplicate samples, add 1.0 mL of spiking solution to 1000 mL aliquots of blank reagent water. Add 250 g of sodium chloride to each sample and shake to dissolve.

- 11.2.3 Add approximately 10 mL of cold 50% sulfuric acid to each sample. Check the pH of the sample(s) with pH paper. If necessary, adjust the pH using additional 50% sulfuric acid to ≤ 2 .
- 11.2.4 For each sample, rinse the sample bottle and graduated cylinder with 120 mL of diethyl ether, and place in the separatory funnel. Seal and shake the separatory funnel vigorously for two minutes with periodic venting to release excess pressure.

CAUTION: Organic solvents can create excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel is vented into a hood to avoid exposure of the analyst to solvent vapors.

- 11.2.5 Allow the ether (top) layer to separate from the water phase. The layers should be visually separate. Drain the water (lower) layer into a clean beaker or Erlenmeyer flask. Collect the ether extract in an Erlenmeyer flask containing some acidified anhydrous sodium sulfate.

NOTE: If the emulsion interface between layers is more than about 1/3 the size of the solvent layer, additional techniques to complete the phase separation must be employed. The optimum technique depends upon the sample and may include slow draining of the solvent, stirring, filtration of the emulsion through glass wool and/or sodium sulfate, or dissolving sodium chloride in the sample.

- 11.2.6 Pour the aqueous phase back into the separatory funnel. Repeat the extraction two more times using fresh 60 mL portions of ether. Combine all extracts in the Erlenmeyer flask.
- 11.2.7 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding additional acidified anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Sample extracts should be dry prior to methylation or else poor recoveries may be obtained (let sit 1½ to 2 hours). Then pass the extract through a filter funnel, containing a folded filter paper containing some sodium sulfate, into the K-D concentrator. Rinse the Erlenmeyer extract flask with 20-25 mL of ether, and pass through the drying funnel into the K-D concentrator. Then rinse the drying funnel with 15-20 mLs of ether.
- 11.2.8 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

CAUTION: Diethyl ether is very volatile and flammable.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

- 11.2.9 When the volume of extract reaches approximately 1 mL, remove the K-D apparatus from the bath and allow to drain and cool. For each extract, add 0.5 of methanol, 1 mL of hexane, and bring to 4 mL volume with ether.
- 11.2.10 Assemble the diazomethane bubbler. Add about 10-12 mL of ether to the first test tube. Add 3 mL of ether, 3 mL of ethoxyethoxy ethanol, 4.5 mL of 37% KOH, and 2 scoops (about 0.5 g) of Diazald to the second test tube. Place the exit tube into the concentrator tube containing the sample extract.

CAUTION: Diazomethane is a carcinogen, and can explode under certain conditions - refer to the MSDS.

NOTE: These amounts are sufficient for derivatization of two samples. Rinse exit tube with ether between samples.

11.2.11 Apply nitrogen flow at about 10 mL/min to bubble diazomethane through the extract for 10 minutes, or until a yellow color persists.

11.2.12 Dilute the extracts to final volume of 10 mL with hexane.

11.2.13 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.3 ULTRASONIC EXTRACTION (METHOD 3550B, except for 8015 WDRO)

11.3.1 Weigh approximately 30 g (*i.e.* 25-35 g) of sample into 500-mL beaker and record the weight to the nearest 0.1 g. Prepare each of the method blank, lab control spike, and matrix spikes using approximately 30 g of sand.

11.3.2 For methods 8081, 8082, 8270, and 8310, add 1.0 mL of the surrogate standard solution to each sample, blank and QC samples. For method 8015 (TPHD), add 50 µL of the surrogate standard solution to each sample, blank and QC samples. Add 1.0 mL of the matrix spike solution to aliquots of the sample chosen for matrix spike and matrix spike duplicate.

11.3.3 Add 100 mL of extraction solvent (methylene chloride for methods 8270, 8310 and 8015 TPHD; 1:1 (v/v) acetone/methylene chloride for methods 8081 and 8082) to each beaker, measuring volumes of solvent using dispenser or volume markings on beakers.

11.3.4 Place the bottom surface of the tip of the disrupter horn below the surface of the solvent, but above the solids layer. Extract ultrasonically for 3 minutes, with the output control knob set at 10 (full power) and with the mode switch on Pulse (not continuous), and percent-duty cycle knob set at 50% (*i.e.* energy on 50% of the time and off 50% of the time).

11.3.5 Decant the extract and filter it through a filter funnel containing a folded filter paper and anhydrous sodium sulfate into a Kuderna-Danish (K-D) apparatus.

11.3.6 Repeat the extraction two more times with two additional 100 mL portions of solvent. After each extraction, filter the extract through the sodium sulfate filter into the K-D apparatus. If the sodium sulfate appears completely hydrated, replace the filter paper and use fresh sodium sulfate. Rinse the filter funnel with about 15-20 mLs of solvent.

11.3.7 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

11.3.8 When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

NOTE: If a solvent exchange is required (for example, hexane for methods 8015, 8081, 8082, and acetonitrile for method 8310), do not remove the K-D apparatus, pour 50 mL of hexane, or 10 mL of acetonitrile, into the top of the Snyder column, and concentrate the extract back down to 1-5 mL. Then remove the K-D apparatus from the bath and allow to drain and cool.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

11.3.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. For method 8310, bring extract to a final volume of 10 mL with acetonitrile. For methods 8015, 8081, 8082, and 8270, use the nitrogen blow-down apparatus to reduce extract volume to 1 mL.

11.3.10 If extract requires cleanup, see appropriate cleanup procedure(s), Section 12.0.

11.3.11 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.3.12 Each soil sample extracted must also have the % dry weight determined. Refer to SOP GLA160BG.

11.4 WDRO SOIL SAMPLE PRESERVATION AND ULTRASONIC EXTRACTION (8015 WDRO)

NOTE: Hexane must be added to soil containers within 72 hours of collection.

11.4.1 Weigh the sample jar and subtract the empty weight to determine the actual soil weight. Record the sample weight in the soil preservation logbook. If the sample weight in a 2 oz jar is >35 grams, or in a 4 oz jar is >70 grams, indicate this in the logbook.

11.4.2 Add hexane to the sample jar in a 1:1 ratio of mL hexane to grams of sample. (If the sample weight is less than 25 g, then add 25 mL hexane.) Add an amount of anhydrous sodium sulfate equal to the sample weight to the sample jar. Spike the sample with 50 µL of WDRO surrogate standard solution. Cap and mix by shaking briefly. Store sample jars in the sample refrigerator until ready for extraction (Section 11.3.3 and following).

11.4.3 WDRO soil sample jars are placed in an water bath and sonicated for 20 minutes. After sonication, the sample extract is filtered through a filter funnel containing a folded piece of filter paper and sodium sulfate into a 200-mL Zymark concentrator tube.

11.4.4 Approximately 30 mL of fresh hexane is added to the sample jar. The jar is capped tightly, placed again in the ultrasonic water bath and sonicated for 20 minutes. After sonication, the contents of the jar are filtered through the filter funnel into the same concentrator tube as the first filtrate. The sample jar is rinsed with about 20-25 mLs of hexane, which is then filtered through the filter funnel.

11.4.5 The concentrator tubes containing the sample extracts are placed into the Turbo Vap II automatic evaporative concentrator, and the evaporation cycle started. The Turbo Vap II automatically concentrates the extract to 1 mL, and then audibly signals that the cycle is complete.

11.4.6 Using a glass Pasteur pipet, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.5 ULTRASONIC EXTRACTION AND DERIVATIZATION FOR HERBICIDES (METHOD 8151)

CAUTION: Notify the Inorganics Department that ether will be in use.

- 11.5.1 For each sample, weigh approximately 30 g (*i.e.* 25-35 g) of sample into a 500-mL beaker and record the weight to the nearest 0.1 g. (For wipe samples, weigh the entire wipe.) Prepare each of the method blank, lab control spike, and matrix spikes using approximately 30 g of sand. Adjust the pH of sample to ≤ 2 with concentrated hydrochloric acid.
- 11.5.2 Add 100 μL of the surrogate standard solution to each sample, blank and QC samples. Add 100 μL of the matrix spike solution to aliquots of the sample chosen for matrix spike and matrix spike duplicate.
- 11.5.3 Add 100 mL of methylene chloride to each beaker, measuring volumes of solvent using dispenser or volume markings on beakers.
- 11.5.4 Place the bottom surface of the tip of the disrupter horn below the surface of the solvent (approximately 0.5 inches), but above the solids layer. Extract ultrasonically for 3 minutes, with the output control knob set at 10 (full power) and with the mode switch on Pulse (not continuous), and percent-duty cycle knob set at 50% (*i.e.* energy on 50% of the time and off 50% of the time).
- 11.5.5 Place the extract in an Erlenmeyer flask. Repeat the extraction two more times with fresh 100 mL portions of methylene chloride. Combine extracts.
- 11.5.6 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding acidified anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Allow the drying agent to remain in contact with the extract for at least 2 hours. Then pass the extract through a filter funnel, containing a folded filter paper containing some acidified anhydrous sodium sulfate, into a K-D concentrator. Rinse the Erlenmeyer extract flask with about 20-25 mL of solvent, and pass through the funnel into the K-D concentrator. Then rinse the funnel with about 15-20 mL of solvent.
- 11.5.7 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.
- 11.5.8 When the volume of extract reaches approximately 5 mL, remove the K-D apparatus from the bath and allow to drain and cool.
- NOTE:** At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.
- 11.5.9 For each sample, place the concentrated extract into a 125-mL separatory funnel. Extract using 15 mL of 12% potassium hydroxide. Shake vigorously for 2 minutes.

CAUTION: Organic solvents can create excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel is vented into a hood to avoid exposure of the analyst to solvent vapors.

11.5.10 Drain the organic (lower) layer into a clean beaker. Drain the aqueous layer into an Erlenmeyer flask. Pour the organic layer back into the separatory funnel. Extract twice more using fresh 15 mL portions of 12% potassium hydroxide. Combine aqueous extracts.

11.5.11 Adjust the pH of the aqueous extract to ≤ 2 with cold 50% sulfuric acid. Place in a clean 125-mL separatory funnel and extract using 40 mL of diethyl ether. Shake vigorously for 2 minutes.

CAUTION: Addition of sulfuric acid to the sample may cause an exothermic reaction. Vent the separatory funnel to release pressure.

11.5.12 Drain the aqueous (lower) layer into a clean beaker. Drain the ether extract layer into an Erlenmeyer flask. Pour the aqueous layer back into the separatory funnel. Extract twice more using fresh 20 mL portions of ether. Combine ether extracts.

11.5.13 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding acidified anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Allow the drying agent to remain in contact with the extract for at least 2 hours. Sample extracts should be dry prior to methylation or else poor recoveries may be obtained. Then pass the extract through a filter funnel, containing a folded filter paper containing some sodium sulfate, into a K-D concentrator. Rinse the Erlenmeyer extract flask with about 20-25 mL of solvent, and pass through the funnel into the K-D concentrator. Then rinse the funnel with about 15-20 mLs of solvent.

11.5.14 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of ether to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

CAUTION: Diethyl ether is very volatile and flammable.

11.5.15 When the volume of extract reaches approximately 1 mL, remove the K-D apparatus from the bath and allow to drain and cool.

11.5.16 Assemble the diazomethane bubbler. Add about 10-12 mL of ether to the first test tube. Add 3 mL of ether, 3 mL of ethoxyethoxy ethanol, 4.5 mL of 37% KOH, and 2 scoops (about 0.5 g) of Diazald to the second test tube. Place the exit tube into the concentrator tube containing the sample extract.

CAUTION: Diazomethane is a carcinogen, and can explode under certain conditions - refer to the MSDS.

NOTE: These amounts are sufficient for derivatization of two samples. Rinse exit tube with ether between samples.

11.5.17 Apply nitrogen flow at about 10 mL/min to bubble diazomethane through the extract for 10 minutes, or until a yellow color persists.

11.5.18 Dilute the extracts to final volume of 10 mL with hexane.

11.5.19 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.6 WASTE DILUTION (METHOD 3580A)

- 11.6.1 Depending on the determinative method requested for the waste dilution sample, a small amount (1-2 g) of sample is mixed in a beaker with approximately 10 mLs of the appropriate solvent. If the sample dissolves in the solvent, the sample can then proceed through the waste dilution procedure (11.4.2). If the sample does not dissolve in the appropriate solvent, then the sample must be extracted as either a water or a soil, depending upon the nature of the sample.
- 11.6.2 Weigh approximately 1 g (0.9 to 1.1 g) of sample into a 250-mL beaker, add 1 mL of the waste dilution surrogate spike solution, and bring to 10 mL final volume with the solvent appropriate for the determinative method. Mix until the sample is fully dissolved. The method blank is 1 mL of the waste dilution surrogate spike solution and 9 mL of solvent mixed in a 250-mL beaker. The blank spike and duplicate are each made by mixing 1 mL of the appropriate spiking solution, 1 mL of the waste dilution surrogate spiking solution, and 8 mL of solvent in 250-mL beakers.
- 11.6.3 If the sample solution requires cleanup, see the appropriate cleanup procedure(s), Section 12.0.
- 11.6.4 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

12.0 CLEANUP PROCEDURES**12.1 SULFURIC ACID CLEANUP (METHOD 3665A)**

- 12.1.1 This cleanup procedure is applicable to sample extracts that are to be analyzed for PCB's only, and which contain observable hydrocarbon contamination, or that have been analyzed and have been shown to contain interfering hydrocarbon contamination. This method uses sulfuric acid for the removal of these substances. The method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.
- 12.1.2 The cleanup procedure is performed in a 4-mL clear glass vial with a Teflon-lined screw cap. One mL of hexane extract and 1 mL of concentrated sulfuric acid are added to the vial, the vial is tightly capped, and then vigorously shaken by hand or on a mechanical shaker for 5 minutes. The solution is then allowed to separate into acid (lower) and hexane (upper) layers. Complete separation of the layers may take between 5 minutes and several hours. Separation can sometimes be expedited by centrifuging the solution. After the layers completely separate, transfer the hexane layer to a new autosampler vial for sulfur cleanup, and proceed with Section 12.2.

12.2 SULFUR CLEANUP (METHOD 3660B)

- 12.2.1 This cleanup procedure is applicable to sample extracts that are suspected to contain dissolved sulfur, or extracts that have been analyzed and have been shown to contain dissolved sulfur. This procedure uses copper powder for the removal of dissolved sulfur.

- 12.2.2 The cleanup procedure is performed directly in the sample extract autosampler vial. Granular copper (20-30 mesh, about 2 g) is added to the 1 mL of extract in the vial to fill about $\frac{1}{4}$ of the vial volume. The vial is capped and shaken vigorously by hand or on a mechanical shaker for 5 minutes. If the shiny surface of the granular copper turns completely black the extract may still contain dissolved sulfur, in which case the extract should be transferred to a new vial, and the procedure repeated with a fresh portion of copper. If the copper has not turned completely black, transfer the cleaned extract to a new labeled autosampler vial for analysis, through a syringe filter attached to a 1-mL Luer-Lok syringe.

12.3 FLORISIL CLEANUP (METHOD 3620B)

CAUTION: Notify the Inorganics Department that ether will be in use.

- 12.3.1 This cleanup procedure is applicable to sample extracts that are to be analyzed for PCB's and/or organochlorine pesticides, and which contain observable hydrocarbon contamination, or that have been analyzed and have been shown to contain interfering hydrocarbon contamination. This procedure is intended only for the cleanup of samples, and not for fractionation. Standardized Florisil must be used for fractionation.
- 12.3.2 Add approximately 20 g of dried Florisil to a 20 mm glass chromatography column. Settle the Florisil by gently tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep.
- 12.3.3 Pre-elute the column with 60 mL of hexane and discard the eluate. Drain the column until the sodium sulfate layer is nearly exposed (*i.e.* solvent drained down to the top of the layer). Quantitatively transfer the sample extract onto the column, completing the transfer using two 1-2 mL rinses with hexane.
- 12.3.4 Place a 500-mL K-D flask equipped with a clean 10-mL concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% diethyl ether in hexane (v/v), using a drip rate of about 5 mL/minute; followed by 200 mL of 15% ether/hexane, and 200 mL of 50% ether/hexane.

NOTE: If the sample is to be analyzed only for PCB's, then only elute with 200 mL of 50% diethyl ether in hexane.

- 12.3.5 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of hexane to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water. When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

CAUTION: Diethyl ether is very volatile and flammable.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

- 12.3.6 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. If necessary, use the nitrogen blowdown apparatus to reduce the extract volume to 1 mL.

- 12.3.7 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

12.4 GEL PERMEATION CLEANUP (METHOD 3640A)

- 12.4.1 Gel permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels to separate molecules of different sizes. For example, GPC cleanup can be used to remove lipids, polymers, copolymers, proteins, and natural resins from samples.

- 12.4.2 Set the flow rate to 5 mL/min of methylene chloride. Switch the flow transfer valve for the eluent to flow to waste.

- 12.4.3 For each sample, prepare a Kuderna-Danish (K-D) apparatus for collection of sample eluent.

- 12.4.4 Retention times of the components of the GPC calibration standards must be checked at least once per week when running this cleanup procedure. Flush and load the sample loop using 1 mL of standard solution. Inject and start the chart recording. Determine and record the retention times for each component. Note elution times for the end of the phthalate peak and the beginning of the sulfur peak.

- 12.4.5 For cleanup of samples, flush and load the sample loop using 1 mL of sample. Inject and start the chart recording. Immediately after the elution time of phthalate, switch the flow transfer valve for eluent to the outlet line leading to the K-D. Just before the elution time of sulfur, switch the valve to transfer flow to waste. Allow sufficient time for sulfur compounds to elute before injection of another sample.

- 12.4.6 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water. When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

NOTE: If a solvent exchange is required (for example, hexane for methods 8081 and 8082), do not remove the K-D apparatus, pour 50 mL of hexane into the top of the Snyder column, and concentrate the extract back down to 1-5 mL. Then remove the K-D apparatus from the bath and allow to drain and cool.

- 12.4.7 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. If necessary, use the nitrogen blowdown apparatus to reduce the extract volume to 0.5 mL.

- 12.4.8 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

13.0 MAINTENANCE AND TROUBLESHOOTING

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation.

14.0 REFERENCES

- 14.1 EPA Method 3500B: Organic Extraction and Sample Preparation.
- 14.2 EPA Method 3510C: Separatory Funnel Liquid-Liquid Extraction.
- 14.3 EPA Method 3550B: Ultrasonic Extraction.
- 14.4 EPA Method 3580A: Waste Dilution.
- 14.5 EPA Method 3620B: Florisil Cleanup.
- 14.6 EPA Method 3660B: Sulfur Cleanup.
- 14.7 EPA Method 3665A: Sulfuric Acid/Permanganate Cleanup.
- 14.8 EPA Method 8015B: Nonhalogenated Organics Using GC/FID.
- 14.9 EPA Method 8081A: Organochlorine Pesticides by Gas Chromatography.
- 14.10 EPA Method 8082: Polychlorinated Biphenyls by Gas Chromatography.
- 14.11 EPA Method 8270C: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS).
- 14.12 EPA Method 8310: Polynuclear Aromatic Hydrocarbons.
- 14.13 EPA Method 8151: Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzoylation Derivatization.
- 14.14 Modified DRO – Method for Determining Diesel Range Organics (Wisconsin DNR).
- 14.15 Great Lakes Analytical Quality Assurance Program manual.
- 14.16 Great Lakes Analytical Chemical Hygiene Plan.
- 14.17 Great Lakes Analytical SOP for Login Department.
- 14.18 Great Lakes Analytical SOP for Hazardous Sample Management.
- 14.19 Gel Permeation Chromatography Cleanup System, Operator's Guide, Waters Chromatography Division, Millipore Corporation.

15.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Manual.

ATTACHMENT 1

SEMIVOLATILES WATER/SOIL EXTRACTION LOG

Page x of 100

Extraction Method _____

Analytical Method _____

Date Extracted _____ by _____

Sample Matrix _____

Date Concentrated _____ by _____

Date Completed _____ by _____

Extraction Solvent _____ Lot _____

Final Solvent _____ Lot _____ by _____

Surrogate Spike Solution No. _____

Matrix Spike Solution No. _____

BATCH No. _____

	Client or ID	Sample No.	Sample Size (mL/g)	Surrogate Volume (mL)	Spike Volume (mL)	pH Adjustment	Solvent Exchange	Final Volume (mL)	Comments/ Cleanups
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
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GREAT LAKES ANALYTICAL

ATTACHMENT 2

EXTRACTION SUMMARY TABLE

	8015D-DR	8015T-TPH-D		8081/8082-Pesticides & PCBs		8151-Herbicides		8270-SVOC		8310-PNA	
Sample Matrix	Aqueous	Aqueous	Solid	Aqueous	Solid	Aqueous	Solid	Aqueous	Solid	Aqueous	Solid
Sample Volume/Weight	1 L	1 L	30 g	1 L	30 g	1 L	30 g	1 L	30 g	1 L	30 g
Sample Preservative	HCl	none		none		none		none		none	
Surrogate Volume	50 µL	50 µL		1 mL		1 mL		1 mL		1 mL	
pH	NA	NA		5-9		≤ 2	≤ 2	1) ≤ 2 2) ≥ 11	NA	NA	
Extraction Solvent	Hexane	MeCl ₂		MeCl ₂	1:1 Acetone - MeCl ₂	Diethyl ether	1) MeCl ₂ 2) KOH 3) Ether	MeCl ₂		MeCl ₂	
Extraction Solvent Volume, mL (Replicates)	60 × 3	60 × 3	100 × 3	60 × 3	100 × 3	120, 60 × 2	1) 100 × 3 2) 15 × 3 3) 40, 20 × 2	1) 60 × 2 2) 60 × 2	100 × 3	60 × 3	100 × 3
Solvent Exchange or Final Solvent	none	Hexane		Hexane		Hexane		none		Acetonitrile	
Volume Solvent Exchange Added	NA	50 mL		50 mL		NA		NA		10 mL	
Nitrogen Blowdown	Yes	Yes		Yes		No		Yes		No	
Extract Final Volume	1 mL	1 mL		1 mL		10 mL		1 mL		10 mL	
Notes						Derivatize with diazomethane		Two extractions at each pH		Fill an additional autosampler vial	

GREAT LAKES ANALYTICAL

**ADDENDUM TO THE LOG-IN STANDARD OPERATING
PROCEDURES**

**STANDARD OPERATING PROCEDURE FOR THE PREPARATION OF SAMPLE
CONTAINERS FOR EPA METHOD 5035**

GLA 5035 BG

REVISION 1.0

Date Approved:

Department Manager:

QA/QC Manager:

Laboratory Manager:

BOTTLE PREPARATION FOR VOLATILES METHOD 5035

The specific bottles supplied by the laboratory for the 5035 method depends on the expected concentration range of the sample. Separate bottles will be supplied for low concentration soil samples and high concentration soil and solid waste samples. The sample vials will be prepared in the laboratory and supplied to our customers.

Low Concentration Soil Samples

1. Add a clean magnetic stirring bar to each clean vial.
2. Add preservative to each vial. The preservative is of 1 gram of sodium bisulfate.
3. Add 5 ml of organic-free reagent water to each vial.
4. Seal the vial with the screw-cap and septum seal.
5. Affix a label to each vial.
6. Weigh the prepared vial to the nearest 0.01 gram, write the weight on the vial.
7. For low level analysis include two to three of these vials along with one methanol preserved container described below as well as a dry weight container.

High Concentration Soil Samples-Collected & Preserved in the Field

1. Add 25 ml of methanol to a clean vial. Label the vial appropriately with contents and date of preparation.
2. Affix a label to a 2 ounce container. Weigh the container to the nearest 0.01 grams. Write the weight on the label.
3. For high level analysis include one methanol vial and container as well as an additional jar for the dry weight determination.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

ANALYSIS OF METALS USING ICP

GLA 6010 BG

Revision 2.1

Approved By:

Department Manager:



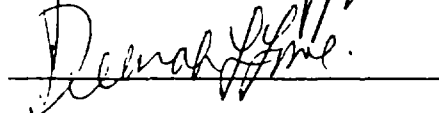
Date: 5/22/99

Quality Assurance Manager:



Date: 5/27/99

Laboratory Director:



Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for analysis of samples for trace metal content by ICP-OES. The procedure for the digestion of liquids is GLA 3015 BG, and for the digestion of solids GLA 3050 BG. This SOP is an interpretation of EPA Methods 200.7, Standard Methods no. 3020, and SW-846 no. 6010B. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to digests prepared for ICP analysis from GLA 3015 BG and GLA 3050 BG. Samples are to be analyzed for metals within 6 months. Drinking water samples are analyzed per SM-3113-B.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

This method describes a technique for the simultaneous (or sequential) multi-element determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the ICP plasma torch where excitation occurs. The plasma torch consists of a flowing stream of argon which is ionized by an applied radio frequency of about 1.1 KW power (0.95-1.15 KW at 27-41 MHz). The field is inductively coupled to the ionized gas by a water cooled coil. Characteristic atomic-line emission spectra are produced by the high temperatures of the plasma torch (6000-8000 K). The spectra are dispersed by a grating spectrophotometer and the intensities of the lines are monitored by photomultiplier tubes. The currents from the photomultiplier tubes are controlled and processed by a computer system. A background correction technique is required to compensate for variable background contributions to the determination of trace elements.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 PLASMA TORCH

The ICP plasma torch produces temperatures of 6000-8000 K and high levels of ultraviolet radiation. All instrument safety interlocks and shields must be in place and operational at all times.

4.0 INTERFERENCES

- 4.1 All water samples must be preserved by the addition of nitric acid to a pH of 2 or less. A low bias could result due to metals adhering to the sides of the sample container or precipitating out of solution.
- 4.2 Spectral interferences can be caused by the overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution, or stray light from the line emission of high-concentration elements. Spectral overlap can be corrected after monitoring the interfering element. Each metal must be optimized and the best wavelength chosen. Unresolved overlap requires selection of another wavelength. Background contribution and stray light can be compensated for by performing background correction. An Interference Check Standard and Blank are analyzed at the beginning and end of each day's analyses, and/or every 8 hours, to evaluate the performance of the instrument.
- 4.3 Changes in viscosity and surface tension can cause significant inaccuracies by interfering with sample flow to the plasma torch, especially in samples containing large amounts of dissolved solids. Physical interferences can be reduced by diluting the sample, by internal standardization with yttrium, or by using standard additions method.
- For internal standardization, yttrium is added at a concentration of 1 ppm to all standards, blanks, and samples by the instrument. Sample intensities are adjusted for changes in yttrium response as a function of the instrument program.
- 4.4 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not substantial with the ICP technique. They can be minimized by careful selection of operating parameters, buffering of samples, matrix matching, and standard addition procedures. Lithium carbonate (200 ppm) is automatically mixed with all standards and samples before analysis for buffering.
- 4.5 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with DI water. Periodic cleaning of sample preparation and analysis areas, will be performed.

5.0 RECORD KEEPING

- 5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.
- 5.2 ICP Log Book:

A log book will be maintained for all metals analyses performed on the ICP. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Sample matrix type
- GLA Sample I.D. (one complete for each set)

- LIMS batch reference number
- LCS and matrix spike information
- Analyst's signature and date analyzed
- Reviewer's signature and date, where applicable
- All dilution factors

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

- 5.3 An instrument log book is also kept for records of scheduled and unscheduled maintenance. All entries must be initialed and dated.
- 5.4 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value. Appendix A contains information on spiking volumes and concentrations.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

6.5 INTERFERENCE CHECKS

The ICP instrument is checked initially and following analytical runs for interferences using an Interference Check Standard and an Interference Check Blank. These are samples containing high concentrations of interfering metals (Al, Ca, Mg, Fe). The Interference Check Standard also contains spiked analytes of interest (Ba, Cd, Cr, Pb, Ag).

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (e.g. a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

8.3 ACCURACY AND PRECISION

Accuracy and precision for this method are tracked by analyzing spike and spike duplicate blanks (sample spikes and duplicates are also analyzed to check for matrix effects). The results are used to establish control limits - average \pm 3 standard deviations for each analyte.

In addition, the ICP instrument is calibrated daily, and the calibration checked using a Check Standard. Each individual analyte calibration must have a correlation coefficient, r^2 , of at least 0.9950 to be usable. The concentrations of the Check Standard must be within 10% of the expected values.

8.4 METHOD DETECTION LIMIT STUDY

8.4.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at $n-1$ degrees of freedom (3.143 for seven replicates).

8.4.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.4.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made, or at least annually.

9.0 EQUIPMENT

9.1 ICP Emission Spectrophotometer, TJA 61E TRACE, Liberty 100, or equivalent

9.2 Volumetric flasks, 25-100 mL size.

9.3 Volumetric pipets, various sizes.

10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II water (DI water). Type I reagent water should be used for the analysis of earth metals and low level lead.

10.2 Nitric acid - concentrated HNO_3 , ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.

10.3 Hydrochloric acid - concentrated HCl , ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.

10.4 Sulfuric acid - concentrated H_2SO_4 - ACS/analytical reagent grade, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.

10.5 Calibration standards - Standards are prepared in 10% nitric acid. Aliquot 1000 ppm individual analyte standards (purchased from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific) for high standard (level 4) per Table 1 into a 100-mL volumetric flask. Add 10 mL of concentrated HNO_3 , dilute to the mark with reagent water, and mix. Prepare the medium standard (level 3) by dilution of the level 4 standard, 10 mL of level 4, 10 mL of concentrated HNO_3 , to 100 mL final volume. Prepare the low standard (level 2) by dilution of the level 3 standard, 10 mL of level 3, 10 mL of concentrated HNO_3 , to 100 mL final volume. The calibration blank (level 1) is prepared by diluting 10 mL of concentrated HNO_3 to 100 mL final volume.

- 10.6 Spiking solutions - GLA-SPK-1A and -4B, purchased from Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. As, Se, Zr standard - 1000 ppm.
- 10.7 Calibration check standard - Add 50 mL of concentrated nitric acid to a 500-mL volumetric flask. Accurately aliquot 1.0 mL each of GLA-SPK-1A, -4B, and -EM into the volumetric flask. Aliquot 1.0 mL each of secondary As, Se, Zr 1000 ppm standards into the flask. Dilute to the mark with reagent water and mix.
- 10.8 Interference check solution - 5000 ppm Al, Ca, Mn, and 2000 ppm Fe, Inorganic Ventures no. CLPP-ICS-A.
- 10.8 Interference check standard ICS-A - Aliquot 50 mL of concentrated sulfuric acid and 50 mL of CLPP-ICS-A into a 500-mL volumetric flask. Dilute to the mark with reagent water and mix.
- 10.9 Interference check standard ICS-B - Aliquot 50 mL of concentrated sulfuric acid and 50 mL of CLPP-ICS-A into a 500-mL volumetric flask. Then, accurately aliquot 1.0 mL each of GLA-SPK-1A, -4B, and -EM into the volumetric flask. Aliquot 1.0 mL each of secondary As, Se, Zr 1000 ppm standards into the flask. Dilute to the mark with reagent water and mix.
- 10.10 Yttrium standard - 10,000 ppm, purchased from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific.
- 10.11 Lithium carbonate - Li_2CO_3 powder, Fisher no. 5840 or Mallinckrodt no. L119.
- 10.12 Buffer/internal standard solution - Weigh approximately 10.7 g of Li_2CO_3 and place in a new, clean 2-L fluorinated plastic bottle. Add 1 L of reagent water. Then add 1.0 mL of 10,000 ppm yttrium standard. Carefully add 200 mL of concentrated HNO_3 . (Solution will effervesce due to release of carbon dioxide.) Dilute to approximately 2 L with reagent water and mix.
- 10.13 Rinse solution - 10% nitric acid in reagent water.

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

NOTE: See Table 1 for the analytes for which this method is applicable. See Appendix B for some recommended wave-lengths, estimated instrumental detection limits (IDL), and potential interferences (at the 100 mg/L level).

11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) *before beginning the analysis*.

Table 1. Preparation and Concentrations of Calibration Standard Solutions.				
ELEMENT	Volume (mL) of 1000 ppm Standard to Prepare High Standard	High Standard (Level 4)	Medium Standard (Level 3)	Low Standard (Level 2)
		Concentration (ppm)	Concentration (ppm)	Concentration (ppm)
Ag	1.0	10.0	1.00	0.100
Al	2.5	25.0	2.50	0.250
As	0.5	5.0	0.50	0.050
B	1.0	10.0	1.00	0.100
Ba	2.5	25.0	2.50	0.250
Be	0.5	5.0	0.50	0.050
Ca	2.5	25.0	2.50	0.250
Cd	0.5	5.0	0.50	0.050
Co	1.0	10.0	1.00	0.100
Cr	1.0	10.0	1.00	0.100
Cu	1.0	10.0	1.00	0.100
Fe	2.5	25.0	2.50	0.250
K	2.5	25.0	2.50	0.250
Mg	2.5	25.0	2.50	0.250
Mn	1.0	10.0	1.00	0.100
Mo	1.0	10.0	1.00	0.100
Na	2.5	25.0	2.50	0.250
Ni	1.0	10.0	1.00	0.100
Pb	0.5	5.0	0.50	0.050
Sb	1.0	10.0	1.00	0.100
Se	0.5	5.0	0.50	0.050
Sn	1.0	10.0	1.00	0.100
Ti	1.0	10.0	1.00	0.100
Tl	1.0	10.0	1.00	0.100
V	1.0	10.0	1.00	0.100
Zn	2.5	25.0	2.50	0.250
Note: See Section 10.5 for complete instructions on calibration standard preparation.				

11.2 INTERFERENCE CHECK STANDARD AND BLANK

An Interference Check Standard, containing high amounts of interfering elements and known concentrations of elements of interest, is analyzed at the beginning and the end of each sequence of samples. The interfering elements are the following concentrations: Al, Ca, Mg - 500 ppm, Fe - 200 ppm. The elements of interest are each spiked at 2.0 ppm (except Ti, which is 4.0 ppm). Recoveries must be within $\pm 20\%$ of the expected concentrations.

An Interference Check Blank, containing high amounts of interfering elements, is analyzed at the beginning and end of each sequence of samples. This blank contains the same concentrations of interfering elements as the check standard. The Interference Blank is analyzed for Ba, Cd, Cr, Pb, and Ag. The concentrations detected for these elements must not be above the reporting limits.

Internal Standard - Yttrium is added at a concentration of approximately 1.0 ppm to all standards, blanks, and samples by the instrument. The intensity is tracked to ensure proper instrument operation.

11.3 INSTRUMENT CALIBRATION

The ICP is calibrated daily before samples are analyzed. The standard curve includes one blank and three standards (4 levels). The correlation coefficient, r^2 , must be at least 0.9950 for each analyte to be run.

The calibration is checked using a Check Standard initially and after every 10 (or fewer) samples. The recovery of the analytes in the Check Standard must be within 10% of expected values. Replicate integrations of the Check Standard must have a %RSD of $\leq 5\%$. For A2LA required work, the High Level Standard (Level 4) is used as a check of the calibration, and must be within $\pm 5\%$ of the actual value.

11.4 OPERATION OF THE INSTRUMENT

- 11.4.1 Power up the instrument and ignite plasma according to the manufacturer's instructions.
- 11.4.2 Allow instrument to warm up at least 30 minutes.
- 11.4.3 Perform system profile in accordance with the manufacturer's instructions using an approximately 5 ppm As standard.
- 11.4.4 Go to analysis section and call up method 6010PM1.
- 11.4.5 Calibrate instrument using calibration standards. Each analyte to be used must have a correlation coefficient of at least 0.9950.
- 11.4.6 Run performance and instrument check samples:

<u>Sample</u>	<u>Criteria</u>
A. ICV (check standard)	$\pm 10\%$
B. ICB (calibration blank)	< reporting limit
C. High standard	$\pm 10\%$
D. ICS-B	$\pm 20\%$
E. ICS-A	< reporting limit (except Al, Ca, Fe, Mg)

- 11.4.7 If all criteria pass, run samples with a CCV and CCB every 10 (or less) samples. The high standard, ICS-B, and ICS-A need to be re-analyzed at the end of the run, or every 8 hours. Each analytical run must end with a calibration blank and a check standard.
- 11.4.8 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used. This procedure involves adding equal volumes of sample to a reagent water blank and to a standard. The higher the degree of accuracy needed, the greater the number of standard additions. The absorbance for each of the prepared solutions is plotted on the vertical axis, with the corresponding standard concentrations plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point at which the line crosses the horizontal axis is the concentration (absolute value) of the sample. The results are considered valid if:
 - the plotted curve is linear over the concentration range of concern (slope should be less than 20% different than the slope of the calibration curve).
 - the effect of the interference does not vary as the ratio of analyte concentration to sample matrix changes and the standard addition responds in a similar manner as the analyte.
 - the determination is free of spectral interferences and corrected for nonspecific background interference.

For a single-addition method, the concentration would be calculated as follows:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where: C_x = Concentration of the sample
 S_B = The analytical signal for the sample and water solution (corrected for the blank)
 V_S = Volume of the standard solution added
 C_S = Concentration of the standard solution added
 S_A = The analytical signal for the sample and standard solution (corrected for the blank)
 V_X = Volume of the sample added to each solution.

Note: V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X , and thus C_S is much greater than C_x , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

11.5 CALCULATIONS

11.5.1 Results are corrected for any spectral interferences and backgrounds (by the instrument software).

11.5.2 All analyte concentrations are multiplied by the applicable dilution factor (DF) to obtain concentrations for the original samples.

For waters/liquids:

$$\text{concentration (mg/L)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times \text{DF}}{\text{initial sample volume (mL)}}$$

For soils/solids/sludges:

$$\text{concentration (mg/kg)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times \text{DF}}{\text{initial sample weight (g)}}$$

To report result in dry weight, divide concentration result by decimal percent solids (e.g. if %solids is 89%, divide by 0.89).

For paints:

$$\text{concentration (\%)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times \text{DF}}{\text{initial sample weight (g)} \times 10,000}$$

10,000 is the factor for converting mg/kg (ppm) to percent.

For wipes:

$$\text{amount (mg per wipe)} = \text{instr. result} \times \text{final digestate volume (mL)} \times \text{DF}$$

To report in mg per square foot, divide result by area (supplied by client).

To convert to μg , multiply result by 1000.

11.5.3 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.5.4 Relative Percent Difference (%RPD) for duplicate analyses:

$$\% \text{ RPD} = \frac{|\text{Conc. of 1}^{\text{st}} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of 1}^{\text{st}} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

12.0 MAINTENANCE AND TROUBLESHOOTING**12.1 GENERAL**

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 CLEANING THE PLASMA TORCH

The plasma torch must be cleaned weekly. This is accomplished by soaking the torch in a solution of 1 part concentrated HCl and 3 parts concentrated HNO₃ overnight. The height of the torch will need adjustment when the torch is replaced.

13.0 REFERENCES

- 13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
- 13.2 Method 3120: Metals by Plasma Emission Spectroscopy, Section B (Inductively Coupled Plasma Method); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
- 13.3 Method SW-846, 3020B: Inductively Coupled Plasma - Atomic Emission Spectroscopy.
- 13.4 Great Lakes Analytical Quality Assurance Program.
- 13.5 Great Lakes Analytical Chemical Hygiene Plan.
- 13.6 Great Lakes Analytical SOP for Login Department.
- 13.7 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Plan.

APPENDIX A.

STANDARD SPIKING LEVELS AND VOLUMES.

	Standard	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume
	GLA-SPK-1A	0.10/100		0.05/50	0.10/50	0.10/50
	GLA-SPK-3B		0.05/50		0.10/50	0.10/50
	GLA-SPK-4B	0.10/100				
	GLA-SPK-5			0.05/50	0.10/50	0.10/50
	GLA-SPK-6					0.10/50
	As/Se Soln.	0.05/50				
	EARTH	0.10/100		0.05/50	0.05/50	

Corresponding Elements and Concentrations (ppm) per matrix

Set	Element	Solid/Soil	D H ₂ O FNC	D H ₂ O ICP	H ₂ O	TCLP/SPLP Ext.
R C R A	Ag	1.0	0.005		0.01	0.51
	As	0.53	0.015		0.03	0.03
	Ba	1.0		0.50	1.0	1.0
	Cd	1.0	0.001		0.002	0.502
	Cr	1.0	0.003	0.50	1.006	1.006
	Hg		0.001		0.001	0.001
	Pb	1.0	0.015		0.03	0.03
	Se	0.28	0.015		0.03	0.03

P R I R T Y	Be	1.0		0.50	1.0	1.0
	Cu	1.0	0.015	0.50	1.03	1.03
	Ni	1.0		0.50	1.0	1.0
	Sb	1.0	0.015	1.0	2.03	2.03
	Tl	2.0	0.015	1.0	2.03	2.03
	Zn	1.0		0.50	1.0	1.0

T A L	Al	1.0		0.5	1.0	1.0
	Co	1.0		0.5	1.0	1.0
	Fe	1.0		0.5	1.0	1.0
	Mn	1.0		0.5	1.0	1.0
	V	1.0		0.5	1.0	1.0

E A R T H	Ca	1.0		1.0	1.0	
	K	1.0		1.0	1.0	
	Li	1.0		1.0	1.0	
	Na	1.0		1.0	1.0	
	Mg	1.0		1.0	1.0	

E X T R A	B	1.0		1.0	2.0	2.0
	Mo	1.0		1.0	2.0	2.0
	Si	1.0		1.0	2.0	2.0
	Sn	1.0		1.0	2.0	2.0
	Ti	1.0		1.0	2.0	2.0

APPENDIX B.

**EXAMPLE WAVELENGTHS, ESTIMATED INSTRUMENTAL DETECTION LIMITS
(IDL), AND POTENTIAL INTERFERENCES AT THE 100 mg/L LEVEL.**

<u>Element</u>	<u>Wavelength (nm)</u>	<u>IDL (µg/L)</u>	<u>Interferent(s) *</u>
Aluminum (Al)	308.215	30	Mn 0.2, V 1.4
Antimony (Sb)	206.833	21	Al 0.5, Cr 2.9, Fe 0.1, Ti 0.3, V 0.5
Arsenic (As)	193.696	35	Al 1.3, Cr 0.4, V 1.1
Barium (Ba)	455.403	0.9	
Beryllium (Be)	313.042	0.2	Ti 0.04, V 0.05
Boron (B)	249.678†	3.8	
Cadmium (Cd)	226.502	2.3	Fe 0.03, Ni 0.02
Calcium (Ca)	317.933	6.7	Cr 0.1, Mn 0.04, Ti 0.03, V 0.03
Chromium (Cr)	267.716	4.7	Mn 0.04, V 0.04
Cobalt (Co)	228.616	4.7	Cr 0.03, Fe 0.01, Ni 0.03, Ti 0.15
Copper (Cu)	324.754	3.6	Ti 0.05, V 0.02
Iron (Fe)	259.940	4.1	Mn 0.1
Lead (Pb)	220.353	28	Al 0.2
Lithium (Li)	670.784	2.8	
Magnesium (Mg)	279.079	20	Cr 0.1, Fe 0.1, Mn 0.3, Ti 0.1, V 0.1
Manganese (Mn)	257.610	0.9	Al 0.01, Cr 0.01
Mercury (Hg)	194.227†	17	
Molybdenum (Mo)	202.030	5.3	Al 0.05, Fe 0.03
Nickel (Ni)	231.604†	10	
Phosphorus (P)	213.618	51	
Potassium (K)	766.491	‡	
Selenium (Se)	196.026	50	Al 0.2, Fe 0.1
Silica (SiO ₂)	251.611	17	
Silver (Ag)	328.068	4.7	
Sodium (Na)	588.995	19	Ti 0.08
Strontium (Sr)	407.771	0.3	
Thallium (Tl)	190.864	27	Al 0.3
Tin (Sn)	189.9890†	17	
Titanium (Ti)	334.941	5.0	
Vanadium (V)	292.402	5.0	Cr 0.05, Fe 0.01, Ti 0.02
Zinc (Zn)	213.856†	1.2	Cu 0.1, Ni 0.3

† second order.

‡ highly dependent on operating conditions and plasma position.

* analyte concentration equivalents.



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METALS
METHOD EXCEPTION (37)

Date Effective: 12/1/98

Supersedes: 1/1/92

Method No.: EPA 6010A

Method Title: Inductively Coupled Plasma Atomic Emission Spectroscopy

The above method is currently being used with the following exceptions:

The following have been added to the analyte list:

Germanium
Tantalum

CAS No.: 7440-56-4
CAS No.: 7440-25-7

THERE ARE NO ADDITIONAL EXCEPTIONS TO THIS METHOD.

Approved by: _____

Date: _____

NOTE:

The above information reflects current modifications to the method.

TITLE: Inductively Coupled Plasma-Atomic Emission Spectroscopy

1.0 SCOPE AND APPLICATION

- 1.1 Inductively coupled plasma-atomic emission spectroscopy (ICP) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.
- 1.2 Elements for which Method 6010 is applicable are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide estimated detection limits for clean aqueous samples using pneumatic nebulization. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

ANALYTE:

CAS

Aluminum	7440-36-0
Al	
Antimony	7440-36-0
Sb	
Arsenic	7440-38-2
As	
Barium	7440-39-3
Ba	
Beryllium	7440-41-7
Be	
Cadmium	7440-43-9
Cd	
Calcium	7440-70-2
Ca	
Chromium	7440-43-9
Cr	
Cobalt	7440-48-4
Co	
Copper	7440-50-8
Cu	
Iron	7439-89-6
Fe	
Lead	7439-92-1
Pb	
Lithium	7439-93-2
Li	
Magnesium	7439-95-4
Mg	
Manganese	7439-96-5
Mn	
Molybdenum	7439-98-7
Mo	
Nickel	7440-02-0
Ni	
Phosphorous	7723-14-0
P	
Potassium	7440-09-7
K	

Selenium	7782-49-2
Se	
Silver	7440-22-4
Ag	
Sodium	7440-23-5
Na	
Strontium	7440-24-6
Sr	
Thallium	7440-28-0
Tl	
Vanadium	7440-62-2
V	
Zinc	7440-66-6
Zn	

INSTRUMENTATION: ICP

2.0 SUMMARY OF METHOD

- 2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Methods 3005-3050). When analyzing for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.
- 2.2 Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Step 8.5.

TABLE 1. RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection	Wavelength(a)(nm)	Estimated Element Limit(b) (ug/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Cadmium	226.502	4
Cesium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7

Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Lithium	670.784	5
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	75
Silver	328.068	7
Sodium	588.995	29
Strontium	407.771	0.3
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

- (a) The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Step 3.1). In time, other elements may be added as more information becomes available and as required.
- (b) The estimated instrumental detection limits shown are taken from Reference 1 in Section 10.0 below. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.
- (c) Highly dependent on operating conditions and plasma position.

3 INTERFERENCES

- 3.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element at the analytical or background measurement wavelengths; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuum or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternative wavelength. Background contribution and stray light can usually be compensated for by a correction adjacent to the analyte line.

Users of all ICP instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Recommended wavelengths are listed in Table 1 and potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

- 3.1.1 Element-specific interference is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately

0.1 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc. The user should be aware of the possibility of interferences other than those specified in Table 2 and that analysts should be aware of these interferences when conducting analyses.

3.1.2 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferent concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

3.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

TABLE 2. ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

Analyte	Wavelength (nm)	Interferent(a,b)									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

(a) Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al - 1000 mg/L
Ca - 1000 mg/L
Cr - 200 mg/L
Cu - 200 mg/L
Fe - 1000 mg/L

Mg - 1000 mg/L
Mn - 200 mg/L
Tl - 200 mg/L
V - 200 mg/L

The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

-
- 3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. Differences in solution volatility can also cause inaccuracies when organic solvents are involved. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Changing the nebulizer and removing salt buildup at the tip of the torch sample injector can be used as an additional measure to control salt buildup. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.
- 3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

- (4.1.1 Computer-controlled emission spectrometer with background correction.
 - 4.1.2 Radio frequency generator compliant with FCC regulations.
 - 4.1.3 Argon gas supply - Welding grade or better.
- 4.2 Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer. For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where spectral interference correction factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
- 4.3 Class A volumetric flasks
- 4.4 Class A volumetric pipets
- 4.5 Analytical balance- capable of accurate measurement to 4 significant figures.

5.0 REAGENTS

- (Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American

Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

5.1.1 Hydrochloric acid (conc), HCl.

5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriate beaker.

5.1.3 Nitric acid (conc), HNO₃.

5.1.4 Nitric acid (1:1), HNO₃. Add 500 mL concentrated HNO₃ to 400 mL water and dilute to 1 liter in an appropriate beaker.

5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hour at 105-C, unless otherwise specified.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the mole fraction and the weight of the metal salt added.

Metal

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

Metal salts

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)} \times \text{mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 1000 ug Al: Dissolve 1.0 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4 mL of (1:1) HCl and 1 mL of concentrated HNO₃ in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.2 Antimony solution, stock, 1 mL = 1000 ug Sb: Dissolve 2.70 g K(SbO)C₄H₄O₆ (mole fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.3 Arsenic solution, stock, 1 mL = 1000 ug As: Dissolve 1.30 g of As₂O₃ (mole fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.4 Barium solution, stock, 1 mL = 1000 ug Ba: Dissolve 1.50 g BaCl₂ (mole fraction Ba = 0.6595), dried at 250-C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.5 Beryllium solution, stock, 1 mL = 1000 ug Be: Do not dry.

- Dissolve 1.77 g $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ (mole fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO_3 , and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.6 Cadmium solution, stock, 1 mL = 1000 ug Cd: Dissolve 1.10 g CdO (mole fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3 . Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.7 Calcium solution, stock, 1 mL = 1000 ug Ca: Suspend 2.50 g CaCO_3 (mole Ca fraction = 0.4005), dried at 180-C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3 . Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.8 Chromium solution, stock, 1 mL = 1000 ug Cr: Dissolve 1.90 g CrO_3 (mole fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.9 Cobalt solution, stock, 1 mL = 1000 ug Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3 . Add 10.0 mL (1:1) HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.10 Copper solution, stock, 1 mL = 1000 ug Cu: Dissolve 1.30 g CuO (mole fraction Cu = 0.7989), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3 . Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.11 Iron solution, stock, 1 mL = 1000 ug Fe: Dissolve 1.40 g Fe_2O_3 (mole fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3 . Cool, add an additional 5.0 mL of concentrated HNO_3 , and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.12 Lead solution, stock, 1 mL = 1000 ug Pb: Dissolve 1.60 g $\text{Pb}(\text{NO}_3)_2$ (mole fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3 . Add 10 mL (1:1) HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.13 Lithium solution, stock, 1 mL = 1000 ug Li: Dissolve 5.324 g lithium carbonate (mole fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.14 Magnesium solution, stock, 1 mL = 1000 ug Mg: Dissolve 1.70 g MgO (mole fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3 . Add 10.0 mL (1:1) concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.15 Manganese solution, stock, 1 mL = 1000 ug Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.16 Molybdenum solution, stock, 1 mL = 1000 ug Mo: Dissolve 2.00 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (mole fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.17 Nickel solution, stock, 1 mL = 1000 ug Ni: Dissolve 1.00 g of

nickel metal, weighed accurately to at least four significant figures. in 10.0 mL hot concentrated HNO₃, cool, and dilute to volume in a 1,000 mL volumetric flask with water.

- 5.3.18 Phosphate solution, stock, 1 mL = 1000 ug P: Dissolve 4.393 g anhydrous KH₂PO₄ (mole fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.19 Potassium solution, stock, 1 mL = 1000 ug K: Dissolve 1.90 g KCl (mole fraction K = 0.5244) dried at 110-C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.20 Selenium solution, stock, 1 mL = 1000 ug Se: Do not dry. Dissolve 1.70 g H₂SeO₃ (mole fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.21 Silver solution, stock, 1 mL = 1000 ug Ag: Dissolve 1.60 g AgNO₃ (mole fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO₃. Dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.22 Sodium solution, stock, 1 mL = 1000 ug Na: Dissolve 2.50 g NaCl (mole fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.23 Strontium solution, stock, 1 mL = 1000 ug Sr: Dissolve 2.415 g of strontium nitrate (Sr(NO₃)₂) (mole fraction 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.24 Thallium solution, stock, 1 mL = 1000 ug Tl: Dissolve 1.30 g TlNO₃ (mole fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.25 Vanadium solution, stock, 1 mL = 1000 ug V: Dissolve 2.30 g NH₄VO₃ (mole fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.26 Zinc solution, stock, 1 mL = 1000 ug Zn: Dissolve 1.20 g ZnO (mole fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO₃. Add 10.0 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.

- 5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Matrix match with the appropriate acids and dilute to 100 mL with water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see Step 5.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should then be scanned using a sequential spectrometer to verify the absence of

inter-element spectral interference in the recommended mixed standard solutions.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo
IV	Al, Ca, Cr, K, Na, Ni, Li, & Sr
V	Ag (see Note to Step 5.4), Mg, Sb, and Tl
VI	P

5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples.

5.5.2 The method blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves (see Step 8.6.1.1 for use). The instrument check standard should be prepared from a source independent from that used in the calibration standards.

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the instrumental detection limits. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

5.8 The quality control sample should be prepared in the same acid matrix as the calibration standards at 10 times the instrumental detection limits and in accordance with the instructions provided by the supplier.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 7.1 See the introductory material in Chapter Three, Metallic Analytes, Steps 3.1 through 3.3.

7.0 PROCEDURE

- 1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Water samples which have been prefiltered and acidified will not need acid digestion as long as the samples and standards are matrix matched. Solubilization and digestion procedures are presented in Sample Preparation Methods (Methods 3005A-3050A).
- 2 Set up the instrument with proper operating parameters established in Step 4.2. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).
- 3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Step 5.4. Flush the system with the calibration blank (Step 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve should consist of a blank and three standards.
- 4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.
- 7.5 Flush the system with the calibration blank solution for at least 1 minute (Step 5.5.1) before the analysis of each sample (see Note to Step 7.3). Analyze the instrument check standard (Step 5.6) and the calibration blank (Step 5.5.1) after each 10 samples.

8.0 QUALITY CONTROL

- 8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for additional quality control procedures.
- 8.2 Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.
- 8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water acidified with the same amounts of acids as were the standards and samples.
- 8.4 Analyze one replicate sample for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. Refer to Chapter One for a more detailed description of an analytical batch.
- 8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Steps 8.5.1 and 8.5.2, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the

instrumental detection limit after dilution), an analysis of a 1:4-dilution should agree within +/- 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

- 8.5.2 Post spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

- 8.6 Check the instrument standardization by analyzing appropriate check standards as follows.

- 8.6.1 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank (Step 5.5.1) and a check standard (Step 5.6).

8.6.1.1 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and reanalyze the previous ten samples.

8.6.1.2 The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

- 8.6.2 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check solution (Step 5.7). Results should be within +/- 20% of the true value obtained in Step 8.6.1.1.

- 8.6.3 Spiked replicate samples are to be analyzed at a frequency of 5% or per analytical batch, whichever is more frequent.

- 8.6.3.1 The relative percent difference between replicate determinations is to be calculated as follows:

$$RPD = \frac{D1 - D2}{(D1 + D2)/2} \times 100$$

where:

RPD = relative percent difference.
D1 = first sample value.
D2 = second sample value (replicate).

(A control limit of +/- 20% RPD shall be used for sample values greater than ten times the instrument detection limit.)

- 8.6.3.2 The spiked replicate sample recovery is to be within +/- 20% of the actual value.

9.0 METHOD PERFORMANCE

- 9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.
- 9.2 In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was 9 +/- 2%. The mean percent recovery of spiked elements for all wastes was 93 +/- 6%. Spike levels ranged from 100 ug/L to 100 mg/L. The wastes included sludges and industrial wastewaters.

10.0 REFERENCES

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TABLE 4. ICP PRECISION AND ACCURACY DATA(a)

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD(b) (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD(b) (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD(b) (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
C	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13

Cd	50	43	12	2.5	2.9	16	14	13	16
Co	700	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

(a) Not all elements were analyzed by all laboratories.

(b) SD = standard deviation.

(c) Results for Se are from two laboratories.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

ANALYSIS OF METALS USING GFAA

GLA 7000 BG

Revision 2.1

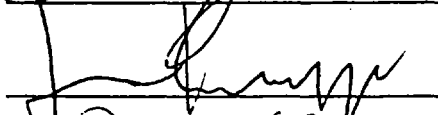
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Department Manager:



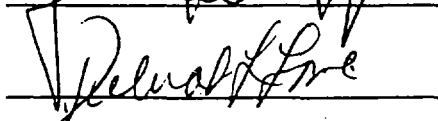
Date: 5/27/99

Quality Assurance Manager:



Date: 5/27/99

Laboratory Director:



Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of samples for trace metal content by graphite furnace atomic absorption (GFAA). The procedure for digestion of liquids is GLA 3015 BG, and for the digestion of solids is GLA 3050 BG. This SOP is an interpretation of EPA Method 200.9, Standard Methods no. 3113, Section B, and SW-846 no. 7000A. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to digests prepared for GFAA analysis from GLA 3015 BG and GLA 3050 BG. Samples must be analyzed within 6 months (liquids preserved with nitric acid). Drinking water samples are analyzed per SM-3113-B.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

Aliquots of the digested samples are spiked with a matrix modifier and placed in the graphite tube via the instrument autosampler. First, a low current heats the tube to dry the sample. The second, or charring stage, destroys organic matter and volatilizes other matrix components at an intermediate temperature. Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomizes the samples. The resultant ground-state atomic vapor absorbs radiation from the hollow cathode lamp, the absorption proportional to the analyte concentration. (See Appendix A for method exceptions.)

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 GRAPHITE FURNACE

The graphite furnace produces ultraviolet radiation. Do not view directly. The magnet of the furnace produces a field of about 8000 gauss RMS during the read stage. Keep pacemakers and magnetic storage media at a minimum distance of 30 cm (12 inches).

4.0 INTERFERENCES

- 4.1 All water samples must be preserved by the addition of nitric acid to a pH of 2 or less. A low bias could result due to metals adhering to the sides of the sample container or precipitating out of solution.
- 4.2 Elemental arsenic and selenium, as well as many of their compounds, are volatile. Samples are susceptible to analyte loss during digestion. Spiked samples are employed to determine whether proper digestion procedures were followed.
- 4.3 Non-specific absorption and light scattering can occur during analyses for arsenic and selenium during the atomization step. Zeeman background correction is used to minimize this effect.
- 4.4 Chlorides (>800 ppm) and sulfate (>200 ppm) interfere with the analysis of selenium. The addition of nickel nitrate as the matrix modifier decreases this interference.
- 4.5 Sometimes an analyte is not completely volatilized and removed from the furnace. This can result in carryover which may be detected by analyses of blanks, and can be decreased by operating the furnace at full power at periodic intervals.
- 4.6 Chemical reaction of elements in the sample with graphite may occur at high temperatures. Elements that form carbides are barium, molybdenum, nickel, silicon, titanium, and vanadium. Using pyrolytically coated tubes minimizes this problem.
- 4.7 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with 50% nitric acid and DI water (see Appendix B). Periodic cleaning of sample preparation and analysis areas, will be performed.

5.0 RECORD KEEPING

- 5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.
- 5.2 GFAA Log Book:

A log book will be maintained for all metals analyses performed on the GFAA. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Sample matrix type
- GLA Sample I.D. (one complete for each set)
- LIMS batch reference number
- LCS and matrix spike information
- Analyst's signature and date analyzed

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

- 5.3 An instrument log book is also kept for records of scheduled and unscheduled maintenance. All entries must be initialed and dated.
- 5.4 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples. (See Appendix C for information on spike volumes and concentrations.)

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

NOTE: For TCLP extracts, the sample matrix spike for As and Se (only) must be at least 50%. Other limits may be applicable per client request. If the recovery falls below this level, the method of standard additions must be used.

6.5 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.6 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

- 7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.
- 7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:
- Client name.
 - Sample numbers.
 - Project name.
 - Matrix.
 - Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

8.3 ACCURACY AND PRECISION

Accuracy and precision for this method are tracked by analyzing spike and spike duplicate blanks (sample spikes and duplicates are also analyzed to check for matrix effects). The results are used to establish control limits - average ± 3 standard deviations for each analyte.

In addition, the GFAA instrument is calibrated at least daily, per each matrix analyzed, and the calibration checked using a Check Standard. The concentrations of the Check Standards must pass within limits indicated in Table 2 (within 10% of the expected values initially, and within 20% thereafter, after every 10 samples).

8.4 METHOD DETECTION LIMIT STUDY

- 8.4.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:
- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.

- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).
- 8.4.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.
- 8.4.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

- 9.1 Atomic Absorption Spectrophotometer, Varian SpectrAA-600Z, computer controlled, with Zeeman correction capacity, or equivalent.
- 9.2 Graphite tube atomizer - GTA 100Z, or equivalent.
- 9.3 Refrigerated water recirculator - set at 20-25°C, Coolflow CFT-33, or equivalent.
- 9.4 Four position lamp turret.
- 9.5 Graphite tubes - pyrolytic coated partition tubes; except use L'vov platform tubes for cadmium analyses.
- 9.6 Autosampler, programmable - PSD 97Z, 50 position, or equivalent.
- 9.7 Volumetric flasks, 25-100 mL.
- 9.8 Volumetric pipettors, adjustable volume.
- 9.9 Sample containers, minimum 100-mL capacity, metal-free.
- 9.10 Analytical balance, calibrated.

10.0 STANDARDS AND REAGENTS

- 10.1 Reagent water - ASTM Type II water (DI water).
- 10.2 Argon gas source at 41 psi.
- 10.3 Nitric acid - concentrated HNO₃, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
- 10.4 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
- 10.5 Sulfuric acid - concentrated H₂SO₄, ACS/analytical reagent grade, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.
- 10.6 Calibration standards - 1000 ppm, for individual analytes, from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific. Prepare stock standard containing 3-6 ppm of analytes of interest, then working standards of 6-60 ppb (see Table 1).
- 10.7 Check standard - 30 ppb, for mid-range concentration. Preparation similarly to standard 10.5.
- 10.8 2% Palladium in nitric acid solution - VHG Labs no. xxx.
- 10.9 1% Nickel in nitric acid solution - VHG Labs no. xxx.
- 10.10 Citric acid - reagent grade, xxx no. xxx.
- 10.11 Ammonium phosphate, dibasic - (NH₄)₂HPO₄, Fisher no. xxx.
- 10.13 Matrix modifiers - for general analytes, use palladium/nickel/citric acid solution. Use appropriate modifiers when necessary for cadmium and silver.
Mixed modifier solution for As, Se, Pb: Aliquot 20 mL of 2% palladium solution, 10 mL of 1% nickel solution, 0.50 g of citric acid and dilute to 100 mL with reagent water.
Phosphate modifier for Cd: Dissolve 1 g of (NH₄)₂HPO₄ in 100 mL of reagent water.
Palladium modifier for Ag: Dilute 20 mL of 2% palladium solution to 100 mL with reagent water.

Table 1. Digestion Methods and Standard Preparations.		
MATRIX	DIGESTION METHOD	STANDARD PREPARED IN
Water Waste water Ground Water ASTM Leachate	3015	10% nitric acid in reagent water
Soil Sludge Solid Wipes Sludge waste Non-aqueous liquids	3050B 3010M	15% nitric acid in reagent water
TCLP Fluid 1	3015	10% nitric acid in TCLP Fluid 1
TCLP Fluid 2	3015	10% nitric acid in TCLP Fluid 2
SPLP Fluid 1	3015	10% nitric acid in SPLP Fluid 1
SPLP Fluid 2	3015	10% nitric acid in SPLP Fluid 2
Air filters	NIOSH 7082	15% nitric acid in reagent water

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

NOTE: Metal analytes for which this method is applicable include: Sb, As, Ba, Cd, Cr, Cu, Pb, Se, Ag, and Tl. (See Appendix D for example wavelengths, instrument detection limits, and concentration ranges.)

11.1 INSTRUMENT PARAMETERS

The following are general instrument parameters. There is a specific hollow cathode lamp for each element. For more detail, consult the manufacturer's operation manual, the maintenance logbook, and the computer generated methods.

11.1.1 Flame Analyses

Parameter	Mn	Fe	K	Cr ⁶⁺
Wavelength	279.5	248.3	766.5	357.9
Fuel	Acetylene	Acetylene	Acetylene	Acetylene
Oxidant	Air	Air	Air	Nitrous Oxide
Type of flame	Slightly oxidizing	Slightly oxidizing	Slightly oxidizing	Fuel Rich
Background correction	Yes	Yes	No	No

11.1.2 Furnace Analyses

Parameter	Pb	As	Se	Tl	Sb	Cd	Cr
Drying Time (sec)/ Temp (°C)	30/120	30/120	30/120	30/120	30/120	30/120	30/120
Ashing Time (sec)/ Temp (°C)	15/800	15/1100	20/900	15/400	20/500	15/400	16/1000
Atomizing Time (sec)/ Temp (°C)	4/2300	5.5/2400	4.1/2400	5.0/2000	5.7/2200	6.0/1600	6.4/2600
Purge Gas	Argon	Argon	Argon	Argon	Argon	Argon	Argon
Wavelength	283.3	193.7	196.0	276.8	217.6	228.8	357.9
Background Corr.	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Note: The above parameters are general. These values could change in order to optimize the instrument for different matrices and other elements.

- 11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) **before beginning the analysis**. The user's manual for the instrument can be consulted for more details on operation of the instrument.

11.2 INSTRUMENT CALIBRATION

- 11.2.1 The GFAA is calibrated daily before samples are analyzed in accordance with the instrument manufacturer's instructions. The standard curve includes one blank and a minimum of three standards, the lowest at or near the method detection limit. Most elements are calibrated using standard concentrations of 10, 20, 40, and 60 µg/L. The calibration must pass with correlation coefficients, r^2 , of at least 0.9950. The instrument performs two attempts to pass calibration before automatically pausing the run.
- 11.2.2 The calibration is checked using a Check Standard initially and after every 10 samples. The recovery of the analytes in the Check Standard must be within 10% of expected values initially, and within 20% thereafter.

11.3 ANALYSIS OF SAMPLES

- 11.3.1 A sequence of QC and test samples is prepared and analyzed:

1. Calibration blank
2. Check standard
3. Check standard
4. High standard
5. Calibration blank
6. 10 Samples
7. Check standard
8. Calibration blank
9. 10 Samples

Note: Each analytical run must end with a calibration blank and a check standard.

Table 2: **Acceptance Criteria for Check Samples**

Calibration blank	< reporting limit
Check standard	±10%, unless second check standard passes
Check standard	±10%, unless first check standard passes
High standard	+10%
Calibration blank	< reporting limit
Continuing check - CCV	±20%
- CCB	< reporting limit

If any parameter fails, the problem must be corrected and tests passed before continuing with samples, including possibly recalibrating the instrument.

- 11.3.2 A standard is run periodically to gauge the lifetime and performance of the graphite tubes. A lack of reproducibility, or a change in the signal for the standard, indicates that tube replacement is due. The ordinary life of a pyrolytic coated graphite tube is approximately 100-350 firings, depending upon the sample matrix and analyte.
- 11.3.3 If the concentration of a sample is greater than the highest standard plus 10%, the sample must be diluted and re-analyzed. The instrument automatically dilutes samples 1:4 and 1:24. If results are still out of range, manual dilutions must be performed.

- 11.3.4 Background correction (Zeeman) must be incorporated at all times. Background correction is important during flameless atomization, especially at wavelengths below 350 nm, and particularly for the analysis of arsenic and selenium in the presence of iron. False positive results may occur from the absorption or scattering of light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam.
- 11.3.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used. This procedure involves adding equal volumes of sample to a reagent water blank and to a standard. The higher the degree of accuracy needed, the greater the number of standard additions. The absorbance for each of the prepared solutions is plotted on the vertical axis, with the corresponding standard concentrations plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point at which the line crosses the horizontal axis is the concentration (absolute value) of the sample. The results are considered valid if:
- the plotted curve is linear over the concentration range of concern (slope should be less than 20% different than the slope of the calibration curve).
 - the effect of the interference does not vary as the ratio of analyte concentration to sample matrix changes and the standard addition responds in a similar manner as the analyte.
 - the determination is free of spectral interferences and corrected for nonspecific background interference.

For a single-addition method, the concentration would be calculated as follows:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_x}$$

where: C_x = Concentration of the sample
 S_B = The analytical signal for the sample and water solution (corrected for the blank)
 V_S = Volume of the standard solution added
 C_S = Concentration of the standard solution added
 S_A = The analytical signal for the sample and standard solution (corrected for the blank)
 V_x = Volume of the sample added to each solution.

Note: V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_x , and thus C_S is much greater than C_x , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

11.4 CALCULATIONS

After a run has been completed and all of the verification standards are in control, the data may be calculated and reported.

11.4.1 Liquid Samples:

$$\text{mg/L} = \text{analyzed concentration} \times \text{dilution factor}$$

Note: For liquids digested using the microwave method, multiply concentrations by the factor 50/45 (= 1.11) to account for dilution of 45 mL of sample with 5 mL of nitric acid.

11.4.2 Solid Samples:

$$\text{mg/kg} = \text{analyzed concentration} \times \text{dilution factor}$$

For solids, multiply concentrations by the factor 100/2 (= 50) to convert from mg/L to mg/kg of sample (from 2 g digested to 100 mL solution, or 1 g to 50 mL for HotBlock digestions). If the sample weight differs substantially from 2 g (or 1 g), use the factor 100/weight (or 50/weight) instead.

11.4.3 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.4.4 Relative Percent Difference (%RPD) for duplicate analyses:

$$\% \text{RPD} = \frac{|\text{Conc. of 1}^{\text{st}} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of 1}^{\text{st}} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. (See Appendix B.) Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 GRAPHITE FURNACE

The graphite shield (shroud) and chimney should be cleaned each time the graphite tube is replaced, using methanol.

The quartz windows should be regularly inspected. To clean, gently remove the windows, wash with 30% methanol, and dry with a Kimwipe. Never use coarse cloths or abrasive cleaning solutions.

The autosampler capillary and syringe should be inspected periodically for wear and damage. Repair or replace when required. Similarly, inspect and replace the electrodes when necessary (for example, when the absorbance peak for a standard begins to shift).

13.0 REFERENCES

- 13.1 EPA Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry.
- 13.2 Method 3113: Metals by Electrothermal Atomic Absorption Spectrometry, Section B (Electrothermal Atomic Absorption Spectrometric Method); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
- 13.3 Method SW-846, 7000: Atomic Absorption Methods.
- 13.4 Great Lakes Analytical Quality Assurance Program.
- 13.5 Great Lakes Analytical Chemical Hygiene Plan.
- 13.6 Great Lakes Analytical SOP for Login Department.
- 13.7 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Manual

APPENDIX A.**METHOD EXCEPTIONS.****A.1 EPA Method 200.9:**

- Section 11.3.3 -The addition of hydrochloric acid in step 11.3.3 has been omitted, and an additional additions of nitric acid are made in its place. The interferences associated with chloride in graphite furnace analysis are well documented (for example, in EPA 200 Series, section 4.1.3).
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

A.2 SM-3030-E:

Additions of acid are made in accordance with SW-846 3010B. The higher concentrations of acid will not compromise the digestion process.

A.3 SW-846 Methods 7060A and 7740A:

The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

A.4 EPA 200 Series, Methods 206.2 and 270.2:

The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

APPENDIX B.**GLASSWARE PREPARATION FOR METAL ANALYSES.**

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

- B.1 All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.
- B.2 Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.
- B.3 All glassware shall subsequently be hand-washed using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.
- B.4 All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.

APPENDIX C.

STANDARD SPIKING LEVELS AND VOLUMES.

Standard	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume
GLA-SPK-1A	0.10/100		0.05/50	0.10/50	0.10/50
GLA-SPK-3B		0.05/50		0.10/50	0.10/50
GLA-SPK-4B	0.10/100				
GLA-SPK-5			0.05/50	0.10/50	0.10/50
GLA-SPK-6					0.10/50
As/Se Soln.	0.05/50				
EARTH	0.10/100		0.05/50	0.05/50	

Corresponding Elements and Concentrations (ppm) per matrix

Set	Element	Solid/Soil	D H ₂ O FNC	D H ₂ O ICP	H ₂ O	TCLP/SP' Ext.
R C R A	Ag	1.0	0.005		0.01	0.51
	As	0.53	0.015		0.03	0.03
	Ba	1.0		0.50	1.0	1.0
	Cd	1.0	0.001		0.002	0.502
	Cr	1.0	0.003	0.50	1.006	1.006
	Hg		0.001		0.001	0.001
	Pb	1.0	0.015		0.03	0.03
	Se	0.28	0.015		0.03	0.03

P R I R T Y	Be	1.0		0.50	1.0	1.0
	Cu	1.0	0.015	0.50	1.03	1.03
	Ni	1.0		0.50	1.0	1.0
	Sb	1.0	0.015	1.0	2.03	2.03
	Tl	2.0	0.015	1.0	2.03	2.03
	Zn	1.0		0.50	1.0	1.0

T A L	Al	1.0		0.5	1.0	1.0
	Co	1.0		0.5	1.0	1.0
	Fe	1.0		0.5	1.0	1.0
	Mn	1.0		0.5	1.0	1.0
	V	1.0		0.5	1.0	1.0

E A R T H	Ca	1.0		1.0	1.0	
	K	1.0		1.0	1.0	
	Li	1.0		1.0	1.0	
	Na	1.0		1.0	1.0	
	Mg	1.0		1.0	1.0	

E X T R A	B	1.0		1.0	2.0	2.0
	Mo	1.0		1.0	2.0	2.0
	Si	1.0		1.0	2.0	2.0
	Sn	1.0		1.0	2.0	2.0
	Ti	1.0		1.0	2.0	2.0

APPENDIX D.

EXAMPLE WAVELENGTHS, DETECTION LEVELS, AND
CONCENTRATION RANGES FOR GFAA.

<u>Element</u>	<u>Wavelength (nm)</u>	<u>IDL (µg/L)</u>	<u>Conc Range (µg/L)</u>
Aluminum (Al)	309.3	3	20-200
Antimony (Sb)	217.6	3	20-300
Arsenic (As)	193.7	1	5-100
Barium (Ba)	553.6	2	10-200
Beryllium (Be)	234.9	0.2	1-30
Cadmium (Cd)	228.8	2	0.5-10
Chromium (Cr)	357.9	1	5-100
Cobalt (Co)	240.7	1	5-100
Copper (Cu)	324.7	1	5-100
Iron (Fe)	248.3	1	5-100
Lead (Pb)†	283.3	1	5-100
Manganese (Mn)	279.5	0.2	1-30
Molybdenum (Mo)	313.3	1	3-60
Nickel (Ni)	232.0	1	5-100
Selenium (Se)	196.0	2	5-100
Silver (Ag)	328.1	0.2	1-25
Tin (Sn)	224.6	5	20-300

† The more sensitive 217.0 nm wavelength is recommended for instruments with background correction capabilities.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY:

CAPILLARY COLUMN METHOD

GLA 8081 BG



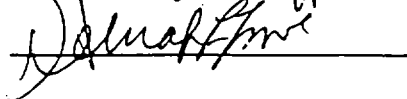
Revision 1.1

Approved By:

Department Manager:

Quality Assurance Manager:

Laboratory Manager:

Date: 5-28-99

Date: 5/23/99

Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of organochlorine pesticides and related compounds by capillary gas chromatography (GC). This SOP is an interpretation of EPA method 8081A. Samples are extracted according to Great Lakes Analytical (GLA) SOP 3500 BG. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for extracts of aqueous, soil/sediment, solid waste, and non-aqueous solvent-soluble waste samples. (Note: use method 8082 for samples for PCB - polychlorinated biphenyl - analysis.) Chlordane and toxaphene are listed as multi-component target analytes. If the matrix of these samples were environmentally degraded (*i.e.* "weathered"), pattern recognition of these analytes may require more detailed study.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

Samples for pesticide analysis are extracted with organic solvents (aqueous samples using separatory funnel liquid-liquid extraction, soil/sediment samples using ultrasonic extraction, GLA SOP 3500 BG, sections 11.1 and 11.3). If necessary, solvent exchange to hexane or isooctane must be performed. Extracts are stored under refrigeration and must be analyzed within 40 days of extraction.

Extracts are analyzed by capillary gas chromatography with electron capture detection (ECD). Electrolytic conductivity detection (ELCD) may also be used. The GC is standardized to determine the recovery and limits of detection for the analytes of interest. Sample concentrations are determined by comparison to standard responses. Quantitative analysis is achieved through measurements of peak heights or integrations of peak areas.

Organochlorine pesticides that can be detected by this method include: aldrin, α -BHC, β -BHC, γ -BHC (lindane), δ -BHC, technical chlordane (including α -chlordane and γ -chlordane), 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, diallate, dieldrin, endosulfans I and II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, isodrin, kepone, methoxychlor, and toxaphene. Other compounds that may be detected include: alachlor, captafol, chloroneb, DCPA, dichlone, dicofol, halowax materials, nitrofen, PCNB, perthane, strobane, permethrin, and trifluralin.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 COMPRESSED GASES

All compressed gases, except air, can cause suffocation by displacing oxygen. Caution should be exercised when changing compressed gas cylinders: Analysts must wear safety glasses when changing cylinders or working with gas plumbing. All compressed gas cylinders must be secured at all times. A handtruck must be used to transport cylinders. The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place.

3.4 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants at high levels. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

4.0 INTERFERENCES

4.1 GLASSWARE

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials are demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Soap residue (for example, sodium dodecyl sulfate), which causes a basic pH on glassware surfaces, may cause degradation of certain analytes. In general, glassware is washed using Contrad or Alconox detergent, and then rinsed thoroughly with organic-free deionized water, acetone, and finally with methylene chloride.

4.2 PLASTICS

Phthalate esters contaminate many types of products found in the laboratory. Plastics, in particular, should not be used because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Substantial phthalate contamination may result at any time if consistent quality control is not practiced. Nitrile gloves must be used.

4.3 COEXTRACTED INTERFERENCES

Materials causing interferences may be coextracted from a sample. The extent of matrix interferences varies from sample to sample. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.

4.4 CARRYOVER

Contamination by carryover can occur whenever samples with high concentration and low concentration are analyzed sequentially. The sample syringe or purging device should be rinsed out between samples with water or solvent to reduce carryover. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or water to check for cross contamination.

4.5 CHROMATOGRAPHY

Coelution among the target analytes may cause interference. For example, DDD and endosulfate II coelute on a DB 608 column, methoxychlor and endosulfan sulfate coelute on a DB1701 column. If this is suspected, standards of the individual analytes may be analyzed and retention times compared.

Carbophenothion, dichlorone, dichloran, nitrofen, and kepone may exhibit extensive peak tailing. Atrazine and simazine may give poor responses on the ECD detector. Triazine compounds should be analyzed using Method 8141 (with NPD option).

4.5 SULFUR

The presence of sulfur produces a large broad peak that interferes with the detection of early to middle eluting analytes. Sulfur contamination should be expected with sediment samples. Since the recovery of sulfur-containing pesticides (e.g. endosulfan, endrin aldehyde) is reduced during sulfur cleanup, these compounds are determined prior to cleanup.

4.6 INDUSTRIAL CHEMICALS

Other pesticides and industrial chemicals (e.g. PCBs) may cause interferences. Some coeluting organophosphorous pesticides can be removed using gel permeation chromatography (GPC) cleanup. Chlorophenols may be removed using florisil cleanup.

5.0 RECORD KEEPING

5.1 INSTRUMENT LOG

Each instrument has an Instrument Log. The instrument identification number and effective dates are written on the front cover. An instrument log is very helpful in tracking problems and is an important troubleshooting guide. Entries in this book include, but are not limited to:

- Installation of the instrument.
- Run parameters for the instrument, autosampler, and data system.
- Instrument and autosampler gas flows.
- All routine and unscheduled maintenance.

5.2 QUALITY CONTROL BOOK

A Quality Control Book is set up for each method. It has the method identification number on the outside cover. The contents of each book include:

- Copy of the GLA Quality Assurance Program manual.
- Copies of GLA SOP and source methods.
- Copies of the calibration studies and the internal standard control limits and dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Copies of all retention time studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Surrogate standard recovery tabulations and control limits.

5.3 RUN LOG

The front cover of the Run Log notebook displays:

- Instrument identification number.
- Method number.
- Run log number.
- Effective dates.

In the front of the notebook record:

- Calculations represented with a generic calculation.
- The names and concentrations of the internal standard and surrogate standard(s).

The following column headings are written at the top of each page:

- Data file name.
- Date.
- Autosampler position.
- Client.
- Full sample number.
- Amount of sample used.
- Matrix type.
- Surrogate standard percent recoveries.
- Results complete with units.
- Comments.

Subsequent information for each sample and standard is then documented under the column headings. Additional documentation concerning standards includes:

- Quality control function (check standard, blank, matrix spike, etc.)
- Concentration.
- GLA code number.
- Recovery.

Each page is dated and signed. Laboratory notebooks must be neat and legible. Mistakes and crossed out with a single line, initialed, and dated. Unused or partial pages are z'ed out.

5.4 STANDARD PREPARATION LOG

When standards are received by the laboratory, the certificate of analysis is dated and placed in the Standards Preparation Certificate of Analysis binder. A log is kept of all standards prepared for the method. Document in the book:

- Analyte, purpose (method, calibration, internal, etc.).
- Supplier.
- Lot number.
- Initial concentration of the stock solution.
- Expiration date of stock standard - 3 months after the standard has been opened, or the date set by manufacturer, whichever is first.
- Initials and date.

Also for working standards:

- Volume diluted.
- Volume prepared.
- Final concentration.
- Expiration of working standard - 6 months after the standard has been prepared, or when the standard fails Quality Control criteria, whichever is first.
- GLA code for the final solution. The GLA code is a number letter sequence used to track standard preparations within the lab. It consists of the month number and successive letter of the alphabet, starting with "A" at the beginning of each month.

6.0 QUALITY CONTROL

6.1 METHOD BLANKS

Method Blanks are prepared and analyzed to check for any laboratory contamination. For each matrix-specific extraction batch, a method blank is prepared. The method blank is taken through the identical extraction steps as the samples. Deionized water and clean sand are used as the blank matrix for water and soil, respectively. No target analytes should be detected above the requested reporting limit. If target analytes are detected in the method blank, and the same target analytes are not found in the samples, no corrective action is taken. If target analytes are detected in the method blank, and the same target analytes are found in the samples, all associated samples and QC are either reextracted, or the results are qualified.

6.2 CHECK STANDARD

Check standards validate the initial calibration curve and is used to gauge the daily operating condition of the instrument. It must be from a different supplier than the calibration standard. The check standards contain the analytes at concentrations of 1 to 100 µg/L. The compounds are quantitated using the average RF for each compound calculated in the calibration study.

The recovery of each analyte in the check standard must be between 85 and 115%.

$$\text{Recovery (\%)} = \frac{\text{calculated concentration}}{\text{concentration analyzed}} \times 100$$

A check standard is analyzed once every 20 samples, or 12 hours, whichever occurs first. The check standard is used to check chromatography for peak shape or co-elution problems. The check standard must be quantitated before the samples in the sequence to verify that the samples are being quantitated against a valid calibration. Recoveries of all check standard analytes are documented in tables for tabulation of yearly statistical recovery limits. Samples must be bracketed by a valid check standard.

6.3 CHECK BLANK

The check blank verifies that the analytical system is free from contamination. No contamination should be present in the blank above the reporting limit. A check blank sample is analyzed once every 20 reportable samples. The check blank must be quantitated before samples to verify that the system is "clean". If contamination is found, samples run in that analysis sequence that contain the same contaminant are reanalyzed with a clean blank to confirm results.

6.4 SURROGATE STANDARD

Surrogate standards are used to monitor the efficiency of the procedure. The surrogate standard for this method is decachlorobiphenyl (TMX = 0.4 µg/mL DCB = 0.3 µg/mL in check standard and 0.5 µg/mL in samples for both). The surrogate standard recoveries are tracked from all standards and samples over a year to determine control limits. These limits are defined as the average recovery plus/minus 3 times the standard deviation. Surrogate standard limits are kept in the QC binder and should be posted by the analyst for reference.

6.5 MATRIX SPIKES

A set of matrix spike/matrix spike duplicates (MS/MSD) are extracted and analyzed regularly to check the effect of the sample matrix on the performance of the method. The MS/MSD is a measure of the accuracy and precision of the method. Samples selected randomly by the LIMS are used for matrix spikes and matrix spike duplicates.

- 6.5.1 An MS/MSD is extracted and analyzed per batch of 20 or less samples of the same matrix. Soil and water matrix spikes samples are spiked with all target compounds (except toxaphene and methoxychlor) at a final concentration of 3.3 µg/Kg and 0.1 µg/L, respectively.
- 6.5.2 Spike recoveries and percent differences of the duplicates for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries and percent differences must fall within the average spike recovery and percent difference over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 10 sets of MS/MSDs. These limits should be posted by the analyst for reference.

6.6 LABORATORY CONTROL SPIKES

The results of the LCS are used to verify the laboratory can perform the analysis in a clean matrix (ie. when MS/MSDs results indicate potential problems due to the sample matrix).

- 6.6.1 An LCS is analyzed with each 12 hour analytical batch. Reagent water (for water LCS) or clean sand (for soil LCS) are spiked with all target compounds (except toxaphene and methoxychlor) at a final concentration of 3.3 µg/Kg and 0.1 µg/L, respectively.
- 6.6.2 Spike recoveries for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 20 LCSs. These limits should be posted by the analyst for reference.

For those extraction batches that do not have sufficient sample volume to extract the matrix spike in duplicate, the LCS is extracted in duplicate.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken to document steps taken to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- Recovery for check standard fails for a particular compound that was present in the sample.
- Decomposition of endrin or DDT exceeds 15%.
- Contamination was present in the blank and in the sample.
- Recovery for QC samples outside of limits.

6.8 CONFIRMATION

All client samples with detected levels of any target compound are re-analyzed on an instrument with a confirmation column (i.e. dissimilar stationary phase to primary column) to verify the presence of the analyte(s). All QC requirements, including calibrations and retention times for the confirmation analyses must be fulfilled. If sensitivity permits, GC/MS method 8270 may be used for confirmation.

6.9 DATA REVIEW

Data obtained by this method are reviewed by another analyst or a supervisor to ensure accuracy of results. (See Data Review Checklist attached to this SOP.)

7.0 SAMPLE MANAGEMENT

- 7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory. Extraction Logbooks contain records of sample extractions and preparations for analytical batches.
- 7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for method 8081 are queued under "EXTR" and "PEST". The information includes:
- Client name.
 - Sample numbers.
 - Project name.
 - Matrix.
 - Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 CALIBRATION STUDY

A calibration study determines the response factors (RFs) for analytes that are used for the determination of concentrations of analytes in samples. A series of different concentrations of analytes is compared to respective peak area responses on a chromatogram. The calibration standard concentrations are 0.05, 0.1, 0.2, 0.5, 0.75, and 1.0 µg/ml. Single point calibrations are performed for multi-component compounds such as toxaphene and technical chlordane.

A response factors (RF) is calculated by tabulating responses of each analyte against the known concentrations of the analytes. The curve is considered linear and an average RF may be used if the relative standard deviation (%RSD) is less than 20%. If the %RSD for any compound is greater than 20%, linear regression is used to establish the equation of the calibration curve for that particular compound: $\text{peak area} = \text{slope} \times \text{concentration} + \text{constant}$. Linear regression is valid only if the correlation coefficient (r^2) is 0.99 or greater.

Procedure summary:

- Prepare and analyze a minimum of 5 concentration levels that span the linear range of the system with the lowest level near, but above, the MDL. Add 0.5 µg/mL of surrogate standard to each level.
- For each compound, calculate:
 - * $RF = \frac{\text{peak area of analyte}}{\text{concentration of analyte}}$
 - * Average and standard deviation for RFs
 - * $\%RSD = \frac{\text{standard deviation of RFs}}{\text{average RF}} \times 100$
- If the %RSD is less than 20%, the average RF value is used.
- If the %RSD is greater than 20%, a calibration curve is generated using linear regression.
- The correlation coefficient for the linear regression must be 0.99 or greater.
- Check standards are analyzed following a calibration study.
- Recovery for the check standards must be between 80 and 120%.

8.2 DETECTION LIMIT STUDY

This study is performed in accordance with the GLA Quality Assurance Program. This study provides the analyst with the minimum detection limit (MDL) for the instrument and analytes. The MDL is defined as the minimum concentration of the analyte that can be measured and reported at a 99% confidence level. The MDL is equal to the standard deviation of the recoveries of 7 aliquots times the t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The t value appropriate for 7 aliquots is 3.143. The calculated MDL must be between 10% and 100% of the concentration of the MDL standard in order for the study to be valid. For example, if you inject 1 µg/L of standard, the calculated MDL must be between 0.1 and 1 µg/L. A MDL study is done annually.

Procedure summary:

- Analyze 7 replicates of low level standard (at or below lowest calibration level standard).
- Calculate standard deviation for the 7 replicates.
- MDL = standard deviation \times 3.143.
- The calculated MDL must be less than the reporting limit.

Note: MDL studies for multi-component compounds (technical chlordane, toxaphene) are defined as the lowest concentration for which pattern recognition is possible.

8.3 RETENTION TIME WINDOW STUDY

The retention time window study is used as a guide for the tentative identification of peaks during sample analyses. A retention time window study is performed annually, or when a new column is installed.

Procedure summary:

- Analyze the check standard three times over a 3 day period.
- Calculate the average retention time and associated standard deviation for each compound.
- For each compound, retention time window = average retention time \pm 3 \times standard deviation. (A standard deviation of 0.01 may be used if the calculated standard deviation is less than 0.01 minutes.)
- If the instrument is equipped with Enviroquant, enter the retention time windows into the initial calibration tables.

8.4 ACCURACY AND PRECISION STUDY

Each new analyst will perform a series of analyses to establish the ability to generate acceptable precision and accuracy (demonstration of proficiency).

Procedure summary:

- Analyze 4 replicate standards or spiked extracts.
- Recoveries of each compound must be between 80 and 120%
- The %RSD must be less than 20%.

9.0 EQUIPMENT

9.1 Gas chromatograph, consisting of:

- Column oven, electron capture detector (ECD) - Hewlett Packard 5890 or equivalent.
- Sample injector/controller - Hewlett Packard 7672 or equivalent.
- Analytical column - 30 m \times 0.53 mm, DB-608 (J&W Scientific, no. 125-6837, or equivalent); for confirmation - 30 m \times 0.25 mm, DB-XLB (J&W Scientific no. 122-1232, or 30 m \times 0.53 mm 0.5 µm XTI-5, or equivalent).
- Data collection and analysis system.

- 9.2 Glass syringes, various sizes.
- 9.3 Volumetric flasks, various sizes.

10.0 STANDARDS AND REAGENTS

10.1 STANDARD SOURCES

Standards can be ordered from EPA or A2LA certified companies. These companies include AccuStandard, Restek, Supelco, and Ultra Scientific. Examples include:

- 10.1.1 Surrogate standard for samples - Restek Pesticide Surrogate Mix (no. 32000): deca-chlorobiphenyl (200 µg/mL); dilute 250 µL to 100 mL with hexane; for waste dilution samples, dilute 750 µL to 25 mL.
- 10.1.2 Spike standards - Restek 608 Pesticide Calibration Mix (no. 32022): xxx; dilute 50 µL to 100 mL with hexane.
- 10.1.3 Analytical method standards -
 - A. Restek Pesticide Standard Mix A (no. 32003): α-BHC, γ-BHC, endosulfan I, heptachlor, 2,4,5,6-tetrachloro-m-xylene (each 8 µg/mL), DDD, DDT, decachlorobiphenyl, dieldrin, endrin (each 16 µg/mL), methoxychlor (80 µg/mL); dilute for a final concentration of 0.1 µg/mL (of each component).
 - B. Restek Pesticide Standard Mix B (no. 32004): aldrin, β-BHC, δ-BHC, α-chlordane, γ-chlordane, heptachlor epoxide, 2,4,5,6-tetrachloro-m-xylene (each 8 µg/mL), DDE, deca-chlorobiphenyl, endosulfan II, endosulfan sulfate, endrin aldehyde, endrin ketone (each 16 µg/mL); dilute for a final concentration of 0.1 or 0.2 µg/mL (for the corresponding 8 and 16 µg/mL components).
 - C. Restek Pesticide Evaluation Mix (no. 32032): aldrin, dibutyl chlorendate, DDT, endrin (each 100 µg/mL); dilute for a final concentration of 1.0 µg/mL (of each component).
- 10.1.4 Final pesticide spike -
Supelco TCL Pesticides Mix (no. 4-8913): aldrin, α-BHC, β-BHC, γ-BHC, δ-BHC, DDD, DDE, DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, methoxychlor (each 2000 µg/mL); dilute for a final concentration of 0.1 µg/mL (of each component).

Note: Standard solutions should be stored protected from light exposure at approximately 4°C in Teflon-sealed containers.

Note: β-BHC, dieldrin, and some other standards may not be adequately soluble in hexane. A small amount of acetone or toluene may be used to dissolve these compounds during preparation of the standard solutions.

Note: Although all single component analytes can be resolved on a new column, two calibration mixtures can be prepared to minimize potential resolution and quantitation problems on older columns and during confirmation analyses. Separate calibration standards are required for each multi-component target analyte (e.g. toxaphene and methoxychlor).

Note: Compounds are also individually available.

10.2 STANDARD DILUTIONS

Stock and working standards should be kept in a refrigerator between 0 and 10°C when not in use to preserve their integrity. **Do not freeze!**

A useful equation for preparations of diluted standards is:

$$C_2 \times V_2 = C_1 \times V_1$$

C_1 = concentration of the stock standard.

C_2 = desired or calculated concentration of the working standard.

V_1 = volume of the stock standard diluted.

V_2 = volume of working standard prepared.

10.3 STOCK STANDARD

Transfer stock standard to a vial and seal with a Teflon-lined cap. Label this vial with:

- Analyte description.
- Manufacturer.
- Lot number.
- Concentration.
- Date opened.
- Expiration date.

Place vial in refrigerator. The stock standard expires 6 months after opening, or the expiration date set by the manufacturer, whichever is first. Opening of the standard is documented in the Standard Log.

10.4 WORKING STANDARD

Standards are prepared in hexane.

- Determine volumes of stock and working standard required.
- Fill volumetric flask about $\frac{3}{4}$ full with hexane.
- Add required volume of stock standard.
- Fill volumetric to the mark.
- Cap and invert three times.
- Transfer to vial with "mini-ner" cap.
- Label vial with:
 - Analyte description.
 - Concentration of standard.
 - Date prepared.
 - Purpose (method).
 - Initials.
 - Expiration date.
 - GLA code.

The working standard expires 6 months after opening, or when the standard fails QC criteria, whichever is first. Preparation is documented in the Standard Log.

NOTE: A 5 μ L aliquot of a 10 ng/ μ L working standard is equivalent to 50 ng:

$$10 \text{ ng}/\mu\text{L} \times 5 \mu\text{L} = 50 \text{ ng}$$

10.5 REAGENTS

10.5.1 Hexane - pesticide grade or equivalent.

10.5.2 Helium - ultra-high purity grade.

10.5.3 Nitrogen - ultra-high purity grade.

11.0 PROCEDURE

NOTE: Method Validation (section 8.0) must be completed before samples can be analyzed. Samples are analyzed in the same manner as method validation solutions.

11.1 ANALYTICAL SEQUENCE

Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded. Calibration of all target analytes must be verified at a minimum of every 12 hours. The calibration factor for each analyte must not exceed a 15% difference when compared to the initial calibration curve.

Example Analytical Sequence:

- Check blank
- Check standard
- No more than 10 samples
- Method spike
- No more than 10 samples
- Method spike duplicate

11.2 RETENTION TIME WINDOWS

11.2.1 Retention time windows are established daily for each analyte. Use the retention times for each analyte in the check standards as the midpoints of the windows. The daily retention time windows are the midpoints plus/minus 3 times the standard deviation (determined in section 8.3). See Appendix A for an example chromatogram.

11.2.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. All client samples with detected levels of any target compound are re-analyzed on an instrument with a confirmation column (dissimilar stationary phase) to verify the presence of the analyte(s). Another technique, such as GC/MS, may be used (see section 11.7).

11.3 GAS CHROMATOGRAPHIC ANALYSIS

11.3.1 GC Operating conditions:

Temperature parameters

Injector: 250°C
Detector: 320°C
Oven program: 50°C for 1 min
50 to 100°C at 25°C/min (2 min)
100 to 320°C at 10°C/min (22 min)
320°C for 1 min
Alternate program for confirmation column:
140°C for 2 min
140 to 240°C at 10°C/min (10 min)
240°C for 8 min
240 to 260°C at 2.5°C/min (8 min)
260°C for 1 min
260 to 280°C at 15°C/min (1.3 min)
280°C for 10 min

Gas flow

Column ~5 mL/min
Make-up ~50 mL/min

Injection

Volume 2 μ L, splitless

The GC column should be conditioned before every pesticide run by injecting a pesticide standard at a concentration of approximately 20 times the daily calibration check. Several analytes, including Aldrin, may be observed in the injection just following this system priming - run an acceptable blank prior to running any standards or samples.

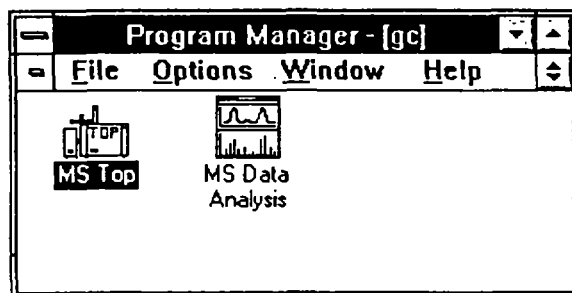
The amount of chemical decomposition of endrin and DDT that occurs within the GC system must be monitored. A standard containing endrin and DDT at concentrations within the calibration range is analyzed. If the amount of decomposition exceeds 15%, take corrective action - usually injection port maintenance.

An initial oven temperature of 140-150°C is required for resolution of the 4 BHC isomers. A final temperature of 240-270°C is required for elution of decachlorobiphenyl.

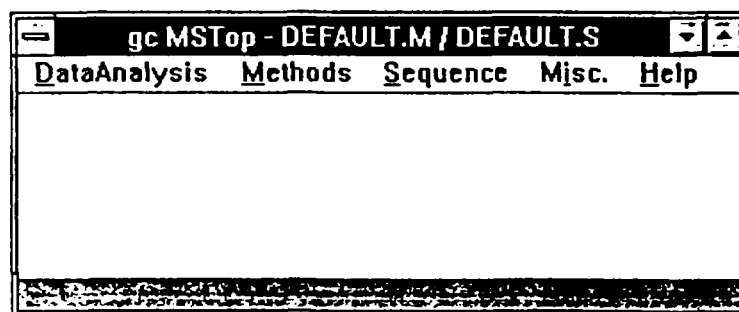
Because of the sensitivity of the ECD detector, the injection port and column should be cleaned prior to calibration.

11.4 SETTING UP A SEQUENCE IN ENVIROQUANT

In Program Manager there is a group called GC-Enviroquant or GC/MS#. Using the mouse, double click to open it and there will be an icon that looks like a GC.



Double click on the GC icon to open it.



Click on the "Sequence" menu item and drag pointer to "Edit Sample Log Table".

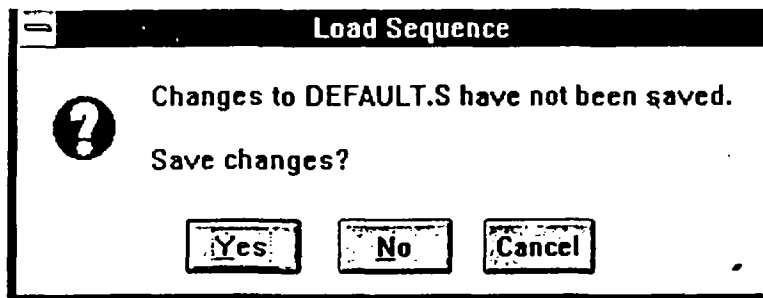
Enter the sample information for each sample including Data File name, Method, and Sample Name. The sample name is the LIMS information, which will look like:

GLA sample number[PEST]8081[OK]

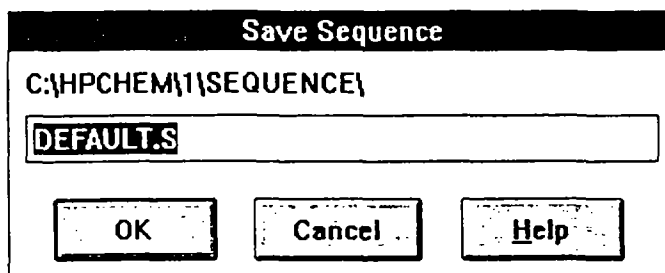
Leave the miscellaneous field empty.

When this is done click on OK.

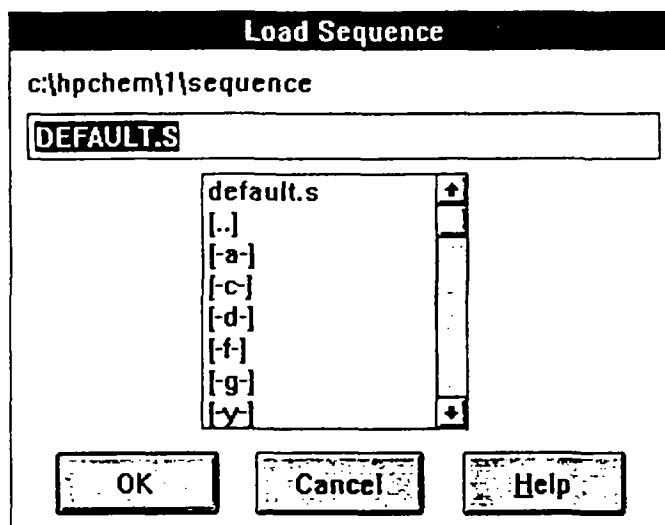
Go back to the "Sequence" menu and drag to "Load and Run Sequence".



Click on "Yes".



Click on "OK".



Click on "OK".

Start Sequence DEFAULT.S Last Modified: Mon Mar 18 18:32:36 1996

Method Sections To Run <input checked="" type="radio"/> Full Method <input type="radio"/> Reprocessing Only	On A Barcode Mismatch <input checked="" type="radio"/> Inject Anyway <input type="radio"/> Don't Inject
--	--

☒ **Overwrite Existing Data Files**

Sequence Comment:

Operator Name:

Data File Directory:

In the "Method Sections To Run" box, the circle next to "Full Method" should be filled in.
 In the "On A Barcode Mismatch" box, the circle next to "Inject Anyway" should be filled in.
 The box next to "Overwrite Existing Data Files" should be checked.
 In the "Operator Name" box, the analyst's initials that are used in LIMS are added.
 In the "Data File Directory" field, after \DATA\, enter today's date or if the sequence was interrupted enter today's date with a letter appendage.
 Click on Run Sequence.

11.5 QUANTITATION

- 11.5.1 If the responses exceed the linear range of the system, dilute the extract and reanalyze. If peak detection is prevented by the presence of interferences, further cleanup is required.
- 11.5.2 The concentration of each analyte in the sample is determined by calculating the amount of standard injected, from the peak response, using the response factor (RF) or linear regression calibration curve (section 8.1). These calculations may be done directly by the data collection and analysis software.

For aqueous samples:

Concentrations determined manually -

$$\text{Concentration } (\mu\text{g/L}) = \frac{A_s \times V_t \times D \times 1000}{CF \times V_s} \quad \text{or} \quad \frac{(A_s - C) \times V_t \times D \times 1000}{S \times V_s}$$

Where:

A_s = peak area response for the analyte in the sample.
 CF = average calibration factor.
 V_t = volume of total extract (1 mL).
 V_s = volume of sample extracted (1000 mL).
 D = dilution factor (if no dilution was made, $D = 1$).
 1000 = factor converting liters to milliliters.
 C = linear regression constant.
 S = linear regression slope.

Concentrations determined by software -

$$\text{Concentration } (\mu\text{g/L}) = \frac{R_s \times V_t \times D \times 1000}{V_s}$$

Where:

R_s = average concentration reported for sample, in μg (divide result by 1000 if concentration reported as mg).

V_t = volume of total extract (1 mL).

V_s = volume of sample extracted (1000 mL).

D = dilution factor (if no dilution was made, $D = 1$).

1000 = factor converting liters to milliliters.

For soil/solid samples:*Concentrations determined manually -*

$$\text{Concentration } (\mu\text{g/kg}) = \frac{A_s \times V_t \times D \times X \times 1000}{CF \times W} \quad \text{or} \quad \frac{(A_s - C) \times V_t \times D \times X \times 1000}{S \times V_s}$$

Where:

A_s = peak area response for the analyte in the sample.

CF = average calibration factor.

V_t = volume of total extract (1 mL).

W = weight of sample extracted (30 g).

D = dilution factor (if no dilution was made, $D = 1$).

X = Percent solids (in decimal form; ex., 90%=0.90)

1000 = factor converting kilograms to grams.

C = linear regression constant.

S = linear regression slope.

Concentrations determined by software -

$$\text{Concentration } (\mu\text{g/kg}) = \frac{R_s \times V_t \times D \times 1000}{W}$$

Where:

R_s = average concentration reported for sample, in μg (divide result by 1000 if concentration reported as mg).

V_t = volume of total extract (1 mL).

W = weight of sample extracted (30 g).

D = dilution factor (if no dilution was made, $D = 1$).

1000 = factor converting kilograms to grams.

11.5.4 If an analyte is not present or present below the reporting limit (RL), report the result as N.D. or "non-detected". However, upon request, analytes detected above the method detection limit (MDL) but below the RL are reported as estimated.

11.5.5 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.5.4 Relative Percent Difference (%RPD) for duplicate analyses:

$$\% \text{RPD} = \frac{|\text{Conc. of 1}^{\text{st}} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of 1}^{\text{st}} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

11.6 MULTI-COMPONENT ANALYTES

Multi-component analytes present problems in measurement. See Appendix B for suggestions for handling toxaphene, strobane, chordane, BHC, and DDT.

11.7 GC/MS CONFIRMATION

11.7.1 GC/MS confirmation may be used in conjunction with either single-column or dual-column analysis if the concentration is sufficient for detection. Full-scan GC/MS will normally require a concentration of approximately 10 ng/μL in the final extract for each single-component compound. Ion trap or selected ion monitoring will normally require a concentration of approximately 1 ng/μL. GC/MS confirmation may not be used for concentrations less than 1 ng/μL. A QC reference sample containing the compounds of interest must be analyzed by GC/MS. The concentration of the QC sample must demonstrate that those pesticides identified by GC/ECD can be confirmed.

11.7.2 GC/MS confirmation should be accomplished by analysis of the same extract that was used for GC/ECD and the associated method blank extract on a calibrated GC/MS instrument. The base/neutral/acid extract and associated blank may be used if the surrogates and internal standards do not interfere and it is demonstrated that the analyte is stable during acid/base partitioning. If the compounds are not detected in the base/neutral/acid extract, the GC/MS analysis of the pesticide extract should be performed.

11.8 REPORTING OF RESULTS

11.8.1 For compound hits that have been confirmed (and are above detection limits):

For aqueous samples:

$$\text{Concentration } (\mu\text{g/L}) = \frac{\text{amount } (\mu\text{g})}{\text{sample}} \times \frac{1 \text{ sample}}{1000 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}}$$

For soil/solid samples:

$$\text{Concentration } (\mu\text{g/kg}) = \frac{\text{amount } (\mu\text{g})}{\text{sample}} \times \frac{1 \text{ sample}}{30 \text{ g}} \times \frac{1000 \text{ g}}{\text{kg}}$$

11.8.2 If an analyte is not present or present below the reporting limit, report the result as N.D. or "non-detected".

11.8.3 Sequences are moved to the reviewed directory on the computer hard drive. The data is reprocessed for the creation of a ".csv" file and this is parsed to the LIMS:

- Go to "tools".
- Go to "do list".
- Quant to forms without cal.
- (OK) -> choose
- Highlight desired files using mouse, and then choose "cancel". Then the next "OK" and files will be created.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be used who may be unsure of the instrumentation and a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 ISOLATE THE PROBLEM

When troubleshooting the system for a chromatography or sensitivity problem, it is important to change only one thing at a time. A standard should be run after every change to see if any progress has been made.

12.4 COLUMN INSTALLATION

Column re-installation is necessary whenever maintenance is performed to the injection or detection ports. A new column is required when the baseline is elevated or the chromatography is poor.

For column installation, first slide the appropriate nuts and ferrules over the ends of the column. Cut 15 cm off both ends of the column by scoring the coating with a sapphire scribe (or equivalent) and breaking the column at the score. Inspect the cut through a magnifying glass to ensure that there are no jagged edges. The proper lengths of the column (to the base of the ferrule nuts) to be inserted into the injection and detection ports are 27 mm and 72 mm, respectively. Mark the placement of the nut with typewriter correction fluid on the column as a point of reference. Tighten the nuts - do not overtighten - make sure the graphite ferrule is seated and not "smashed".

New columns must be conditioned before method validation: Leave the column disconnected from the detection port. Ramp the oven temperature up to just below its maximum, at 1°C/min, and hold for 4 hours.

13.0 REFERENCES

- 13.1 EPA Method 8000B: Gas Chromatography.
- 13.2 EPA Method 8081A: Organochlorine Pesticides by Capillary Column Gas Chromatography.
- 13.3 Great Lakes Analytical Quality Assurance Program manual.
- 13.4 Great Lakes Analytical Chemical Hygiene Plan.
- 13.5 Great Lakes Analytical SOP for Login Department.
- 13.6 Great Lakes Analytical SOP for Hazardous Sample Management.

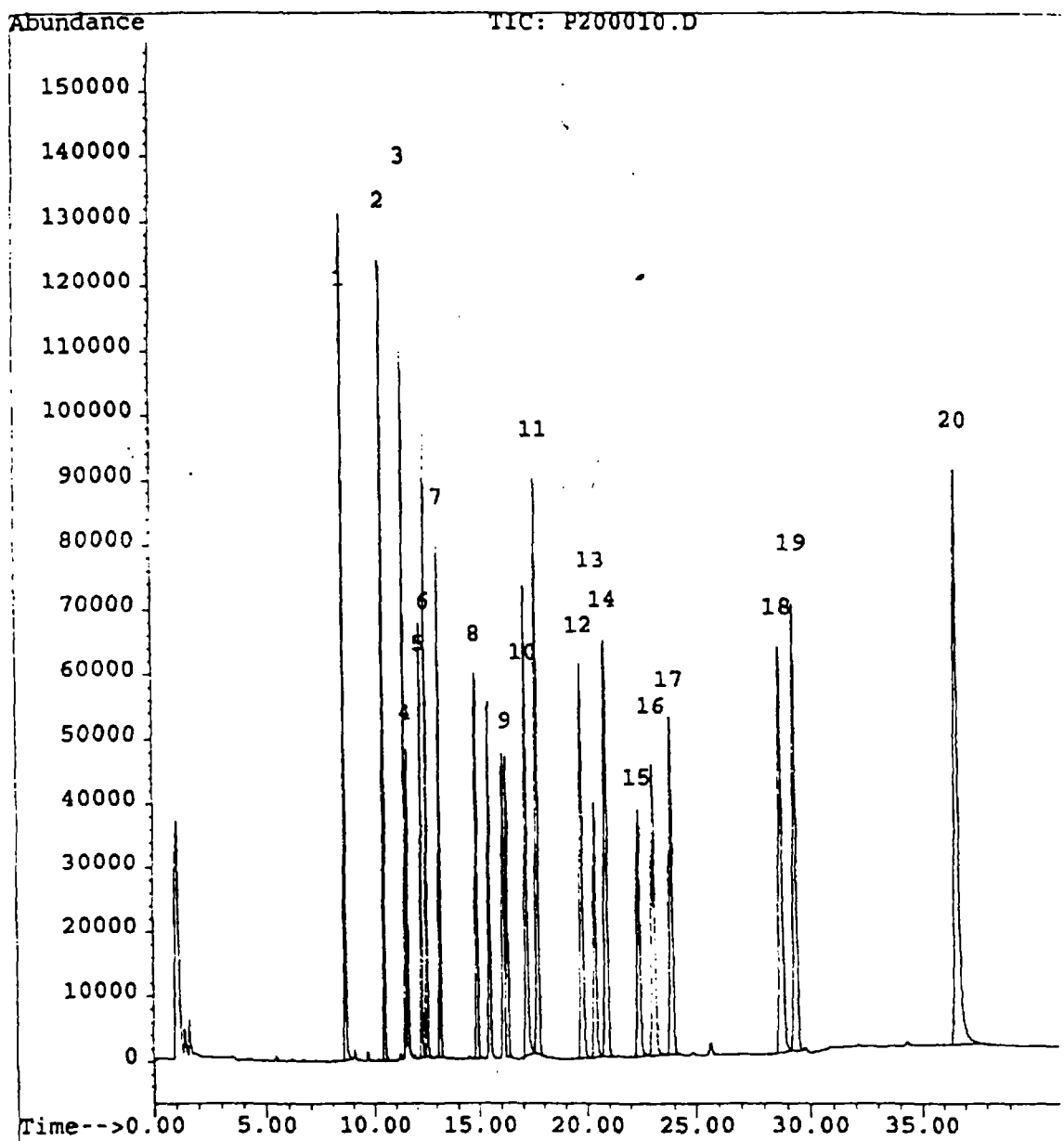
14.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Manual.

APPENDIX A.

EXAMPLE CHROMATOGRAM.

<u>Peak No.</u>	<u>Compound</u>	<u>Approximate R.T. (min)</u>	<u>Response (area counts $\times 10^6$)</u>
1	Tetrachloro-m-xylene	8.6	5.7
2	α -BHC	10.5	4.6
3	γ -BHC (lindane)	11.5	3.8
4	β -BHC	11.6	1.6
5	Heptachlor	12.3	2.7
6	δ -BHC	12.5	3.6
7	Aldrin	13.2	3.6
8	Heptachlor epoxide	14.9	3.2
9	Endosulfan I	16.3	2.8
10	4,4'-DDE	17.2	5.2
11	Dieldrin	17.7	6.3
12	Endrin	19.8	5.1
13	4,4'-DDD	20.4	3.3
14	Endosulfan II	20.9	5.6
15	4,4'-DDT	22.4	3.3
16	Endrin aldehyde	23.1	4.3
17	Endosulfan sulfate	23.9	4.8
18	Methoxychlor	28.8	6.3
19	Endrin ketone	29.4	6.2
20	Decachlorobiphenyl	36.6	11.1



APPENDIX B.

ANALYSIS OF MULTI-COMPONENT ANALYTES.

- A.1 **Toxaphene** - Toxaphene is manufactured by the chlorination of camphenes, whereas strobane results from the chlorination of a mixture of camphenes and pinenes. For the calculation of toxaphene:

- Adjust the sample size so that the major toxaphene peaks are 10-70% of full scale.
- Inject a toxaphene standard that is estimated to be within 10 ng of the sample amount.
- Quantitate using the 5 major peaks or the total area of the toxaphene pattern:

To measure total area, construct the baseline of standard toxaphene between its extremities and construct the baseline under the sample peaks, using the distances of the peak troughs to baseline on the standard as a guide. The relative heights and widths of the peaks in the sample may not be identical to the standard.

A series of toxaphene residues have been calculated using the total peak area for comparison to the standard and also using the area of the last 4 peaks only, in both sample and standard. The agreement between the results obtained by the 2 methods justifies the use of the latter method for calculating toxaphene in a sample where the early eluting portion of the toxaphene chromatogram shows interferences from other substances such as DDT.

- A.2 **Chlordane** - Chlordane is a technical mixture of at least 11 major and 30 minor components. *Trans*- and *cis*-chlordane (α and γ , respectively), are the 2 major components of chlordane. The exact percentage of each component is not consistent from batch to batch.

The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factor such as water and sunlight.

Whenever possible, when a chlordane residue does not resemble chlordane, the analyst should quantitate the peaks of α -chlordane, γ -chlordane, and heptachlor separately against the appropriate reference materials, and report the individual results.

When the GC pattern of the residue resembles that of technical chlordane, the analyst may quantitate chlordane residues by comparing the total area of the chlordane chromatogram using the 5 major peaks or the total area. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected chlordane area.

To measure the total area of the chlordane chromatogram, inject an amount of a technical chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms.

Note: Octachloro epoxide, a metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.

- A.3 **Hexachlorocyclohexane** - Hexachlorocyclohexane consists of a mixture of 6 chemically distinct isomers of benzene hexachloride (BHC) and one or more heptachloro- and octachloro-cyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer (α , β , γ , and δ) separately against a standard of the respective pure isomer.
- A.4 **DDT** - Technical DDT consists primarily of a mixture of 4,4'-DDT (~75%) and 2,4'-DDT (~25%). As DDT weathers, 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, and 2,4'-DDD are formed. Since the 4,4'- isomers of DDT, DDE, and DDD predominate in the environment, these are the isomers normally regulated by the EPA. Sample extracts should be quantitated against standards of the respective pure isomers of 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD.

DATA REVIEW

		YES	NO	CA	FLAG
1	Check standard recoveries within $\pm 15\%$?				
(8081) 1b	Prime and blank run?				
(8081) 1c	Endrine DDT breakdown < 15 % ?				
(8270) 1d	DFTPP tune evaluated and passing? \				
(8270) 1e	SPCC average response factor > 0.050 ?				
(8270) 1f	CCC % deviation > 20 % ?				
(8270) 1g	Internal recoveries within 50-100 % ?				
2	Method blank recoveries < reporting limits? *				
3	LCS within control limits?				
4	MS/MSD within control limits?				
5	All surrogate recoveries within control limits?				
6	All hits out of cal range diluted and re-analyzed?				
7	All sample holding times met?				
8	No transcription errors?				
9	No calculation errors?				

COMMENTS:

Analyst review signature: _____

Date: _____

**Method Detection Limits (MDL), Practical Quantitation Limits (PQL), and
Reporting Limits (RL)**
Method: Pesticides by 8081

Analyte	Water (µg/L)			Soil (µg/Kg)		
	MDL	PQL	RL	MDL	PQL	RL
alpha-BHC	0.0034	0.012	0.025	0.073	0.26	0.25
gamma-BHC	0.0023	0.008	0.025	0.077	0.27	1
beta-BHC	0.0033	0.012	0.025	0.121	0.43	1
Heptachlor	0.0037	0.013	0.025	0.051	0.18	1
delta-BHC	0.0018	0.007	0.025	0.082	0.29	1
Aldrin	0.0046	0.016	0.025	0.150	0.53	1
Heptachlor epoxide	0.0018	0.007	0.025	0.053	0.19	1
Endosulfan 1	0.0087	0.031	0.05	0.137	0.49	1
4,4-DDE	0.0032	0.011	0.025	0.057	0.20	2
Dieldrin	0.0026	0.009	0.01	0.046	0.16	2
Endrin	0.0011	0.004	0.05	0.060	0.21	2
4,4-DDD	0.0048	0.017	0.05	0.133	0.47	2
Endosulfan 11	0.0017	0.006	0.05	0.103	0.36	2
4,4-DDT	0.0040	0.014	0.05	0.095	0.34	2
Endrin aldehyde	0.0027	0.010	0.05	0.055	0.19	2
Endosulfan sulfate	0.0052	0.018	0.05	0.134	0.48	2
Methoxychlor	0.0130	0.046	0.5	0.863	3.06	20
Chlordane (*)	0.1	N/A	0.5	3.33	N/A	20
Toxaphene (*)	0.5	N/A	2	16.6	N/A	80

(*)--This compound is a multi-component analyte. The MDL for this analyte is based on the lowest concentration at which pattern recognition can be performed.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

POLYCHLORINATED BIPHENYLS BY GAS CHROMATOGRAPHY: ✓

CAPILLARY COLUMN METHOD

GLA 8082 BG

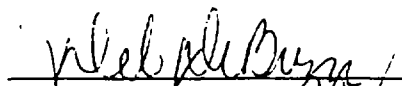

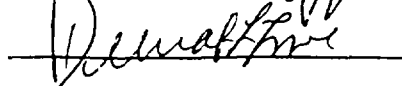
Revision 1.1

Approved By:

Department Manager:

Quality Assurance Manager:

Laboratory Manager:

Date: 5-28-99

Date: 5/28/99

Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of polychlorinated biphenyls (PCBs) and related compounds by capillary gas chromatography (GC). This SOP is an interpretation of EPA method 8082. Samples are extracted according to Great Lakes Analytical (GLA) SOP 3500 BG. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for extracts of aqueous, soil/sediment, solid waste, and non-aqueous solvent-soluble waste samples. Use method 8081 for samples for organochlorine pesticide analysis. If the matrix of these samples were environmentally degraded (*i.e.* "weathered"), pattern recognition of these analytes may require more detailed study.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

Samples for PCB analysis are extracted with organic solvents (aqueous samples using separatory funnel liquid-liquid extraction, soil/sediment samples using ultrasonic extraction, see GLA SOP 3500 BG, sections 11.1 and 11.3).

Extracts are analyzed by capillary gas chromatography with electron capture detection (ECD). The GC is standardized to determine the recovery and limits of detection for the analytes of interest. Sample concentrations are determined by comparison to standard responses. Quantitative analysis is achieved through measurements of peak heights or integrations of peak areas.

This method is used to determine the concentrations of PCBs as Aroclors (mixtures). PCBs that can be detected by this method include Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260. The Aroclors are composed of various mixtures of 2-chlorobiphenyl, 2,3-dichlorophenyl, and the various isomers (congeners) of tri-, tetra-, penta-, hexa-, hepta-, and nona-chlorobiphenyls.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents, chemicals, and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 COMPRESSED GASES

All compressed gases, except air, can cause suffocation by displacing oxygen. Caution should be exercised when changing compressed gas cylinders. Analysts must wear safety glasses when changing cylinders or working with gas plumbing. All compressed gas cylinders must be secured at all times. A handtruck must be used to transport cylinders. The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place.

3.4 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

4.0 INTERFERENCES

4.1 GLASSWARE

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials are demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Soap residue (for example, sodium dodecyl sulfate), which causes a basic pH on glassware surfaces, may cause degradation of certain analytes. In general, glassware is washed using Contrad or Alconox detergent, and then rinsed thoroughly with organic-free deionized water, acetone, and finally with methylene chloride.

4.2 PLASTICS

Phthalate esters contaminate many types of products found in the laboratory. Plastics, in particular, should not be used because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Substantial phthalate contamination may result at any time if consistent quality control is not practiced. Nitrile gloves must be used.

4.3 COEXTRACTED INTERFERENCES

Materials causing interferences may be coextracted from a sample. The extent of matrix interferences varies from sample to sample. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.

4.4 CARRYOVER

Contamination by carryover can occur whenever samples with high concentration and low concentration are analyzed sequentially. The sample syringe or purging device should be rinsed out between samples with solvent to reduce carryover. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross contamination.

4.5 COELUTION

Coelution among the target analytes may cause interference. If this is suspected, standards of the individual analytes may be analyzed and retention times compared.

4.5 SULFUR

The presence of sulfur can result in broad peaks that interfere with the detection of early-eluting analytes. Sulfur contamination should be expected with sediment samples. Since the recovery of sulfur-containing pesticides (e.g. endosulfan) is reduced during sulfur cleanup, this compound is determined prior to cleanup.

4.6 INDUSTRIAL CHEMICALS

Other pesticides and industrial chemicals may cause interferences. For example, some coeluting organophosphorous pesticides can be removed using gel permeation chromatography (GPC) cleanup.

5.0 RECORD KEEPING

5.1 INSTRUMENT LOG

Each instrument has an Instrument Log. The instrument identification number and effective dates are written on the front cover. An instrument log is very helpful in tracking problems and is an important troubleshooting guide. Entries in this book include, but are not limited to:

- Installation of the instrument.
- Run parameters for the instrument, autosampler, and data system.
- Instrument and autosampler gas flows.
- All routine and unscheduled maintenance.
- Date and initials of analyst performing work.

5.2 QUALITY CONTROL BOOK

A Quality Control Book is set up for each analysis. It has the method identification number on the outside cover. The contents of each book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copies of the calibration studies and the internal standard control limits and dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Copies of all retention time studies and dates in use.
- Spike and spike duplicate recovery tabulations and control limits.
- Surrogate standard recovery tabulations and control limits.

5.3 RUN LOG

The front cover of the Run Log notebook displays:

- Instrument identification number.
- Method number.
- Run log number.
- Effective dates.

In the front of the notebook record:

- Calculations represented with a generic calculation.
- The name and concentration of the surrogate standard.

The following column headings are written at the top of each page:

- Data file name.
- Date.
- Autosampler position.
- Client.
- Full sample number.
- Amount of sample used.
- Matrix type and method.
- Results complete with units.
- Comments.
- Analyst.

Each page is initialed and dated. Laboratory notebooks must be neat and legible. Mistakes are crossed out with a single line, initialed, and dated. Unused or partial pages are z'ed out.

5.4 STANDARD PREPARATION LOG

A log is kept of all standards prepared for the method. Document in the book:

- Analyte, purpose (method, calibration, internal, etc.).
- Supplier.
- Lot number.
- Initial concentration of the stock solution.
- Expiration date of stock standard - 6 months after the standard has been opened, or the date set by manufacturer, whichever is first.
- Initials and date.

Also for working standards:

- Volume diluted.
- Volume prepared.
- Final concentration.
- Expiration of working standard - 6 months after the standard has been prepared, or when the standard fails Quality Control criteria, whichever is first.
- GLA code(s) for the final solution(s). The GLA code is an alphanumeric sequence used to track standard preparations within the lab in a method-type-date-(letter) format. For example, "8270 CAL 020599 A" indicates method 8270, calibration standard, prepared 2/5/99, first concentration level (A).

6.0 QUALITY CONTROL

6.1 METHOD BLANKS

Method Blanks are prepared and analyzed to check for any laboratory contamination. For each matrix-specific extraction batch, a method blank is prepared. The method blank is taken through the identical extraction steps as the samples. Deionized water and clean sand are used as the blank matrix for water and soil, respectively. No target analytes should be detected above the requested reporting limit. If target analytes are detected in the method blank, and the same target analytes are not found in the samples, no corrective action is taken. If target analytes are detected in the method blank, and the same target analytes are found in the samples, all associated samples and QC are either reextracted, or the results are qualified.

6.2 INSTRUMENT BLANK

The instrument blank verifies that the analytical system is free from contamination - no contamination should be present in the blank above the reporting limit. The instrument blank must be quantitated before samples to verify that the system is "clean". If contamination is found, corrective action must be initiated. For example, samples run in that analysis sequence which contain the same contaminant are reanalyzed with a clean blank to confirm results, or the results flagged to indicate possible contamination.

6.3 CHECK STANDARD

Check standards validate the initial calibration curve and are used to gauge the daily operating condition of the instrument. The check standards contain the analytes at concentrations within the calibration range (mid-range). Periodically, a high or low standard may be used for this. The peaks are quantitated using the average RF for each compound calculated in the calibration study. Aroclor mixture 1016/1260 is used for initial verification of calibration (CCV).

The recovery of each peak in the check standard must be between 85 and 115 (100 ± 15) %. If the average recovery of the entire compound list is $100 \pm 15\%$, then the method is considered "in calibration" for all compounds.

$$\text{Recovery (\%)} = \frac{\text{calculated concentration}}{\text{concentration analyzed}} \times 100$$

A check standard is analyzed once at a minimum of every 20 samples or every 12 hours. Each analytical run must end with the analysis of a check standard. The check standard is used to check chromatography for peak shape or co-elution problems. The check standard must be quantitated before the samples in the sequence to verify that the samples are being quantitated against a valid calibration. All sequences must be bracketed with passing check standards. Recoveries of all check standard analytes are documented in tables for tabulation of yearly statistical recovery limits.

6.4 SURROGATE STANDARD

Decachlorobiphenyl is employed as a surrogate standard to monitor the efficiency of the procedure. 0.5 µg of surrogate standard is added to all QC and test samples before extraction. The surrogate standard recoveries are tracked from all samples over a year to determine control limits. These limits are defined as the average recovery plus/minus 3 times the standard deviation. Surrogate standard limits are kept in the QC binder and should be posted by the analyst for reference.

6.5 MATRIX SPIKES

A set of matrix spike/matrix spike duplicates (MS/MSD) are extracted and analyzed regularly to check the effect of the sample matrix on the performance of the method. The MS/MSD is a measure of the accuracy and precision of the method. Samples selected randomly by the LIMS are used for matrix spikes and matrix spike duplicates.

- 6.5.1 An MS/MSD is extracted and analyzed per batch of 20 or less samples of the same matrix. Soil and water matrix spikes samples are spiked with Aroclor 1016/1260 mixture at a final concentration of 33 µg/Kg and 1.0 µg/L, respectively.
- 6.5.2 Spike recoveries and percent differences of the duplicates for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries and percent differences must fall within the average spike recovery and percent difference over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 10 sets of MS/MSDs. These limits should be posted by the analyst for reference.

6.6 LABORATORY CONTROL SPIKES (LCS)

The results of the LCS are used to verify the laboratory can perform the analysis in a clean matrix (ie. when MS/MSDs results indicate potential problems due to the sample matrix).

- 6.6.1 An LCS is analyzed with each 12 hour analytical batch. Reagent water (for water LCS) or clean sand (for soil LCS) are spiked with Aroclor 1016/1260 mixture at a final concentration of 33 µg/Kg and 1.0 µg/L, respectively.
- 6.6.2 Spike recoveries for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 20 LCSs. These limits should be posted by the analyst for reference.

For those extraction batches that do not have sufficient sample volume to extract the matrix spike in duplicate, the LCS is extracted in duplicate.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken to document steps taken to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- Recovery for check standard fails.
- Contamination was present in the blank and in the sample.
- Recovery for QC sample outside of limits.

6.8 CONFIRMATION

All client samples with detected levels of any target compound are re-analyzed on an instrument with a confirmation column to verify the presence of the PCB(s). If sensitivity permits, GC/MS method 8270 may be used for confirmation (Full-scan GC/MS will normally require a minimum concentration of 10 ng/ μ L in the final extract for each single-component compound. GC/MS may not be used for confirmation when concentrations are less than 1 ng/ μ L in the extracts.) All QC requirements, including calibrations and retention time windows, must be fulfilled for the confirmation analyses. If the confirmation result differs from the original result by more than 40% and there is no evidence of chromatographic anomalies or interferences, then the higher value is reported, and the client is notified of the possible problem.

6.9 DATA REVIEW

Data obtained by this method are reviewed by another analyst or a supervisor to ensure accuracy of results. (See Data Review Checklist attached to this SOP.)

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory. Extraction Logbooks contain records of sample extractions and preparations for analytical batches.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for method 8082 are queued under "EXTR" and "PCBS". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 INITIAL CALIBRATION

A calibration study determines the calibration factors (CFs) for analytes that are used for the determination of concentrations of analytes in samples. A series of different concentrations of analytes is compared to respective peak area responses on a chromatogram.

An Aroclor 1016/1260 mixture is used to demonstrate linearity of detection. A minimum of 5 concentration levels are used (a minimum of 5 representative peaks in each chromatogram are used for Aroclor identification and quantitation). The concentrations of the calibration standards are 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 µg/ml. A mid-range concentration standard is used for single-point calibration for PCBs other than 1016 and 1260.

Calibration factors (CF) are calculated by tabulating responses of each peak against the known concentrations of the analytes. The curve is considered linear and an average RF may be used if the relative standard deviation (%RSD) is less than 20%. If the %RSD for any compound is greater than 20%, linear regression (not forced through the origin, nor including the origin as a data point) is used to establish the equation of the calibration curve for that particular peak: $\text{peak area} = \text{slope} \times \text{concentration} + \text{constant}$. Linear regression is valid only if the correlation coefficient (r^2) is 0.99 or greater.

Procedure summary:

- Prepare and analyze a minimum of 5 concentration levels that span the linear range of the system with the lowest level near, but above, the MDL. Add surrogate standard (0.05-1.0 µg/mL of TMX+DCB) to each level.
- For each peak, calculate:
 - * $CF = \frac{\text{peak area of analyte}}{\text{concentration of analyte}}$
 - * Average and standard deviation for CFs
 - * $\%RSD = \frac{\text{standard deviation of CFs}}{\text{average RF}} \times 100$
- If the %RSD is less than 20%, the average CF value is used.
- If the %RSD is greater than 20%, a calibration curve is generated using linear regression.
- The correlation coefficient for the linear regression must be 0.99 or greater.
- Check standards are analyzed following a calibration study.
- Recovery for the check standards must be between 85 and 115%.

8.2 DETECTION LIMIT STUDY

This study is performed in accordance with the GLA Quality Assurance Program. This study provides the analyst with the minimum detection limit (MDL) for the instrument and analytes. The MDL is defined as the minimum concentration of the analyte that can be measured and reported at a 99% confidence level. The MDL is equal to the standard deviation of the concentrations determined for 7 spiked samples multiplied by the "t value" appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The t value appropriate for 7 samples is 3.143. The calculated MDL must be between 10% and 100% of the concentration of the MDL standard in order for the study to be valid. For example, if 0.20 µg/L of standard is injected, the calculated MDL must be between 0.02 and 0.20 µg/L. A MDL study is performed annually.

Procedure summary:

- Analyze 7 replicates of a spiked sample with low level standard (at or below lowest calibration level standard).
- Calculate the standard deviation for the results for the 7 replicates.
- Each MDL = standard deviation \times 3.143.
- The calculated MDLs must be between 10 and 100% of the MDL standard.

(MDLs for Aroclors should vary in the range of 0.05 to 0.9 µg/L in water, and 57 to 70 µg/kg in soils.)

Note: MDL studies for multi-component compounds, such as the aroclors, are defined as the lowest concentration for which pattern recognition is possible. However, a traditional MDL study as described above is performed for the Aroclor 1016/1260 mixture.

8.3 RETENTION TIME WINDOW STUDY

The retention time window study is used as a guide for the tentative identification of peaks during sample analyses. A retention time window study is performed when a new column is installed, or annually.

Procedure summary:

- Analyze the check standard three times over a 3 day period.
- Calculate the average retention time and associated standard deviation for each compound.
- For each compound, retention time window = average retention time \pm 3 \times standard deviation.
- If the instrument is equipped with Enviroquant, enter the retention time windows into the initial calibration tables.

8.4 ACCURACY AND PRECISION STUDY

Each new analyst will perform a series of analyses to establish the ability to generate acceptable precision and accuracy.

Procedure summary:

- Analyze 4 replicate standards or spiked extracts.
- Recoveries of each compound must be between 70 and 130%.
- The %RSDs must be less than 20%.

9.0 EQUIPMENT

9.1 Gas chromatograph, consisting of:

- Column oven, electron capture detector (ECD) - Hewlett Packard 5890 or equivalent.
- Sample injector/controller - Hewlett Packard 7672 or equivalent.
- Analytical column - 30 m \times 0.53 mm, DB-608 (J&W Scientific, no. 125-6837, or equivalent).
- Data collection and analysis system.

9.2 Glass syringes, various sizes.

9.3 Volumetric flasks, various sizes.

10.0 STANDARDS AND REAGENTS

10.1 STANDARD SOURCES

Standards can be ordered from EPA or A2LA certified companies. These companies include AccuStandard, Restek, Supelco, and Ultra Scientific. Examples of standards include:

- 10.1.1 Surrogate standard - Restek Surrogate (no. 32000): deca-chlorobiphenyl (200 μ g/mL); dilute 250 μ L to 100 mL with acetone, for waste dilution samples, dilute 750 μ L to 25 mL with acetone.
- 10.1.2 Spike standard - Mixture of Aroclors 1016 and 1260 at 1.0 μ g/mL each.
- 10.1.3 Check standards (1000 μ g/mL, in hexane, from Restek) -
 - A. Aroclor 1221 (no. 32007)
 - B. Aroclor 1232 (no. 32008)
 - C. Aroclor 1242 (no. 32009)
 - D. Aroclor 1248 (no. 32010)
 - E. Aroclor 1254 (no. 32011)
 - F. Aroclor 1260 (no. 32012)
 - G. Working check standard - dilute 50 μ L of 1000 μ g/mL standard(s) to 50 mL with hexane.

10.1.4 Calibration standards (1000 µg/mL, in hexane, from Supelco) -

- A. Aroclor 1016 (no. 90123R)
- B. Aroclor 1221 (no. 90124R)
- C. Aroclor 1232 (no. 90125R)
- D. Aroclor 1242 (no. 90126R)
- E. Aroclor 1248 (no. 90127R)
- F. Aroclor 1254 (no. 90128R)
- G. Aroclor 1260 (no. 90129R)

10.2 STANDARD DILUTIONS

Stock and working standards should be kept in a refrigerator between 0 and 10°C when not in use to preserve their integrity.

A useful equation for preparations of diluted standards is:

$$C_2 \times V_2 = C_1 \times V_1$$

C_1 = concentration of the stock standard.

C_2 = desired or calculated concentration of the working standard.

V_1 = volume of the stock standard diluted.

V_2 = volume of working standard prepared.

10.3 STOCK STANDARD

Transfer stock standard to a vial and seal with a Teflon-lined cap. Label this vial with:

- Analyte description.
- Manufacturer.
- Lot number.
- Concentration.
- Date opened.
- Expiration date.

Place vial in refrigerator. The stock standard expires 3 months after opening, or the expiration date set by the manufacturer, whichever is first. Opening of the standard is documented in the Standard Log.

10.4 WORKING STANDARD

Standards are prepared in hexane.

- Determine volumes of stock and working standard required.
- Fill volumetric flask about ¾ full with hexane.
- Add required volume of stock standard.
- Fill volumetric to the mark.
- Cap and invert three times.
- Transfer to vial with "mini-ner" cap.
- Label vial with:
 - Analyte description.
 - Concentration of standard.
 - Date prepared.
 - Purpose (method).
 - Initials.
 - Expiration date.
 - GLA code.

The working standard expires 6 months after opening, or when the standard fails QC criteria, whichever is first. Preparation is documented in the Standard Log.

NOTE. A 5 μ L aliquot of a 10 ng/ μ L working standard is equivalent to 50 ng:
 $10 \text{ ng}/\mu\text{L} \times 5 \mu\text{L} = 50 \text{ ng}$

10.5 REAGENTS

10.5.1 Hexane - pesticide grade or equivalent.

10.5.2 Helium - ultra-high purity grade.

10.5.3 Nitrogen - ultra-high purity grade.

11.0 PROCEDURE

NOTE: Method Validation (section 8.0) must be completed before samples can be analyzed. Samples are analyzed in the same manner as method validation solutions.

11.1 ANALYTICAL SEQUENCE

Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with verification of instrument calibration, followed by sample extracts interspersed with QC samples, and ends with a check standard. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

11.2 RETENTION TIME WINDOWS

11.2.1 Retention time windows are adjusted daily using the results for each analyte in the check standard.

11.2.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. All client samples with detected levels of any target compound are re-analyzed on an instrument with a confirmation column (e.g. a dissimilar column) to verify the presence of the analyte(s).

11.3 GAS CHROMATOGRAPHIC OPERATING CONDITIONS

Temperature parameters

Injector: 250°C

Detector: 320°C

Oven program: 140°C for 2 min
140 to 240°C at 10°C/min (10 min)
240°C for 8 min
240 to 260°C at 2.5°C/min (8 min)
260°C for 1 min
260 to 280°C at 15°C/min (1.3 min)
280°C for 10 min

Gas flow

Column ~5 mL/min

Make-up ~50 mL/min

Injection

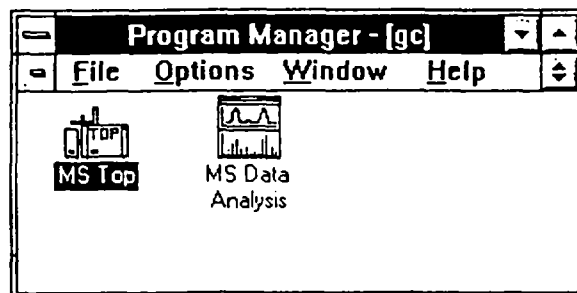
Volume 2 μ L, splitless

See Figures 1 and 2 for example chromatograms.

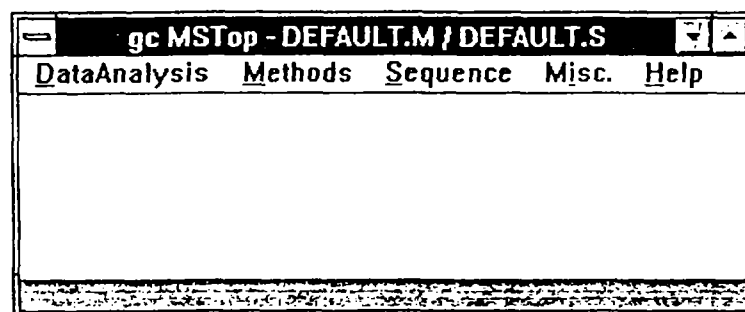
NOTE: Chromatographic conditions may be adjusted to give adequate separation of the characteristic peaks in each Aroclor. Once established, the same operating conditions are used for analysis of samples and standards.

11.4 SETTING UP A SEQUENCE IN ENVIROQUANT

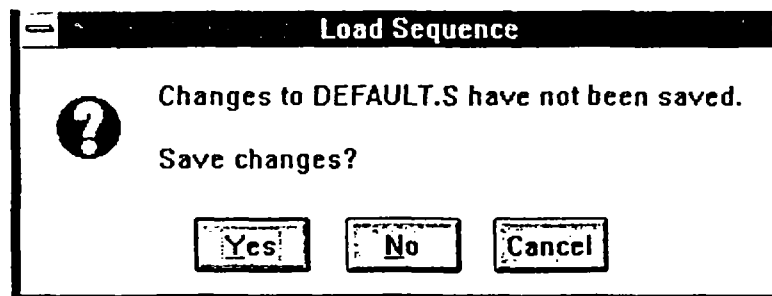
In Program Manager there is a group called GC-Enviroquant or GC/MS-#. Using the mouse, double click to open it and there will be an icon that looks like a GC.



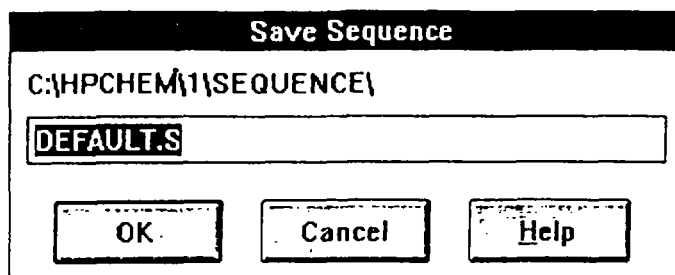
Double click on the GC icon to open it. (Note: Actual screen displays "GC Top" and "GC Data Analysis" icons.)



Click on the "Sequence" menu item and drag pointer to "Edit Sample Log Table". Enter the sample information for each sample including Data File name, Method, and Sample Name. The sample name is the LIMS information, which will look like:
GLA sample number|PCBS|8082|OK
Leave the miscellaneous field empty.
When this is done click on OK.
Go back to the "Sequence" menu and drag to "Load and Run Sequence".



Click on "Yes".



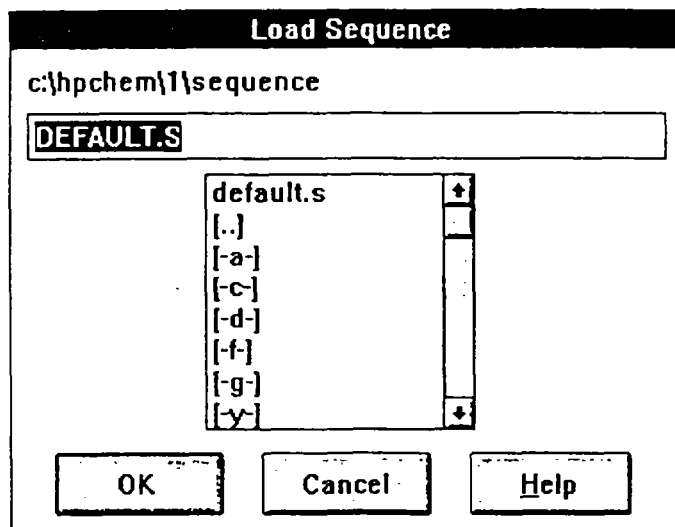
Save Sequence

C:\HPCHEM\1\SEQUENCE\

DEFAULT.S

OK Cancel Help

Click on "OK".



Load Sequence

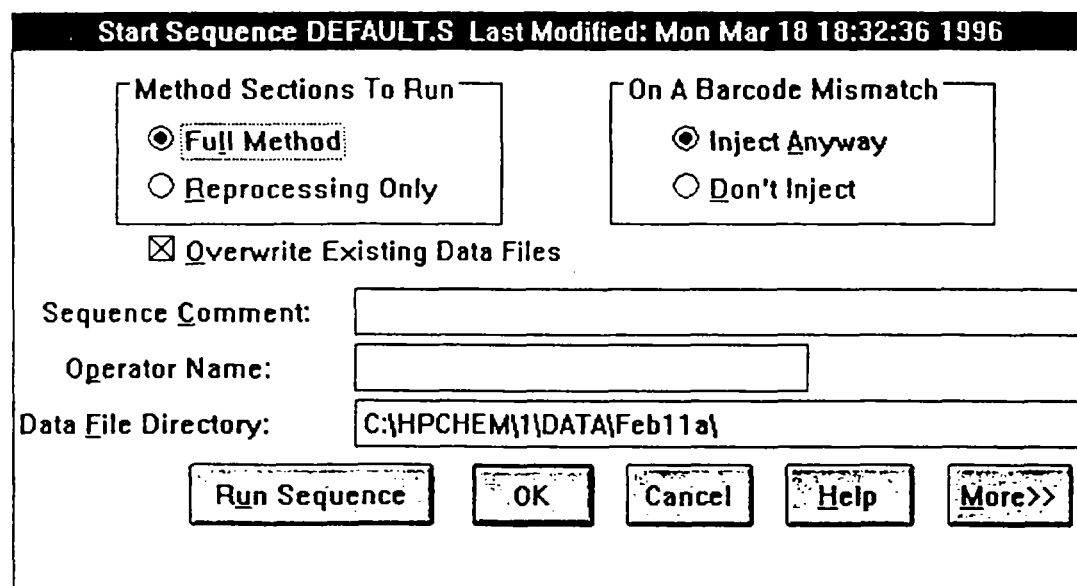
c:\hpchem\1\sequence

DEFAULT.S

default.s
[.]
[-a-]
[-c-]
[-d-]
[-f-]
[-g-]
[-y]

OK Cancel Help

Click on "OK".



Start Sequence DEFAULT.S Last Modified: Mon Mar 18 18:32:36 1996

Method Sections To Run

☒ Full Method
☐ Reprocessing Only

☒ Overwrite Existing Data Files

On A Barcode Mismatch

☒ Inject Anyway
☐ Don't Inject

Sequence Comment:

Operator Name:

Data File Directory: C:\HPCHEM\1\DATA\Feb11a\

Run Sequence OK Cancel Help More>>

In the "Method Sections To Run" box, the circle next to "Full Method" should be filled in.
In the "On A Barcode Mismatch" box, the circle next to "Inject Anyway" should be filled in.
The box next to "Overwrite Existing Data Files" should be checked.
In the "Operator Name" box, the analyst's initials that are used in LIMS are added.

In the "Data File Directory" field, after \DATA\, enter today's date or if the sequence was interrupted enter today's date with a letter appendage.
Click on Run Sequence.

11.5 QUANTITATION

- 11.5.1 When analyzing for Aroclors, a minimum of 3 peaks must be chosen for each Aroclor for pattern recognition. At least one of three peaks must be unique to the Aroclor of interest. At least 5 peaks are used for identity of Aroclor 1016/1260 mix. Every attempt should be made to avoid manual integration. If absolutely necessary, it must be performed in a manner which is consistent with the integration of the standards used for calibration. The manipulation of integration parameters in a way that is inconsistent with the integration of standards constitutes fraud and is strictly forbidden.
- 11.5.2 If the responses exceed the concentration of the upper calibration standard, dilute the extract and reanalyze. If peak detection is prevented by the presence of interferences, further cleanup is required.
- 11.5.3 For reporting compounds that have been confirmed, the concentration of each analyte in the sample is determined by calculating the amount of standard injected, from the peak response, using the average calibration factor (CF) or linear regression calibration curve (section 8.1). These calculations may be done directly by the data collection and analysis software.

For aqueous samples:

Concentrations determined manually -

$$\text{Concentration } (\mu\text{g/L}) = \frac{A_s \times V_t \times D \times 1000}{CF \times V_s} \quad \text{or} \quad \frac{(A_s - C) \times V_t \times D \times 1000}{S \times V_s}$$

Where:

- A_s = peak area response for the analyte in the sample.
- CF = average calibration factor.
- V_t = volume of total extract (1 mL).
- V_s = volume of sample extracted (1000 mL).
- D = dilution factor (if no dilution was made, D = 1).
- 1000 = factor converting liters to milliliters.
- C = linear regression constant.
- S = linear regression slope.

Concentrations determined by software -

$$\text{Concentration } (\mu\text{g/L}) = \frac{R_s \times V_t \times D \times 1000}{V_s}$$

Where:

- R_s = average concentration reported for sample, in μg (divide result by 1000 if concentration reported as mg).
- V_t = volume of total extract (1 mL).
- V_s = volume of sample extracted (1000 mL).
- D = dilution factor (if no dilution was made, D = 1).
- 1000 = factor converting liters to milliliters.

For soil/solid samples:*Concentrations determined manually -*

$$\text{Concentration } (\mu\text{g/kg}) = \frac{A_s \times V_t \times D \times X \times 1000}{CF \times W} \quad \text{or} \quad \frac{(A_s - C) \times V_t \times D \times X \times 1000}{S \times V_s}$$

Where:

A_s = peak area response for the analyte in the sample.

CF = average calibration factor.

V_t = volume of total extract (1 mL).

W = weight of sample extracted (30 g).

D = dilution factor (if no dilution was made, D = 1).

X = Percent solids (in decimal form; ex., 90% = 0.90)

1000 = factor converting kilograms to grams.

C = linear regression constant.

S = linear regression slope.

Concentrations determined by software -

$$\text{Concentration } (\mu\text{g/kg}) = \frac{R_s \times V_t \times D \times 1000}{W}$$

Where:

R_s = average concentration reported for sample, in μg (divide result by 1000 if concentration reported as mg).

V_t = volume of total extract (1 mL).

W = weight of sample extracted (30 g).

D = dilution factor (if no dilution was made, D = 1).

1000 = factor converting kilograms to grams.

- 11.5.4 If an analyte is not present or present below the reporting limit (RL), report the result as N.D. or "non-detected". However, upon request, analytes detected above the method detection limit (MDL) but below the RL are reported as estimated.

11.5.5 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.5.4 Relative Percent Difference (%RPD) for duplicate analyses:

$$\% \text{ RPD} = \frac{|\text{Conc. of 1}^{\text{st}} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of 1}^{\text{st}} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

11.6 PARSING DATA TO LIMS

All PCB analyses are manually entered into LIMS, based on pattern recognition and quantitation.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 ISOLATE THE PROBLEM

When troubleshooting the system for a chromatography or sensitivity problem, it is important to change only one thing at a time. A standard should be run after every change to see if any progress has been made.

12.4 INJECTION PORT

When maintenance of the injection port is indicated, for example, by a loss of resolution and/or peak response. The port should be cleaned with hexane, and all replaceable parts exchanged. The column may also be checked for slugs of grease, etc., and these portions of the column removed.

12.5 COLUMN INSTALLATION

Column re-installation is necessary whenever maintenance is performed to the injection or detection ports. A new column is required when the baseline is elevated or the chromatography is poor (e.g. poor peak shape and/or low response).

For column installation, first slide the appropriate nuts and ferrules over the ends of the column. Cut 15 cm off both ends of the column by scoring the coating with a sapphire scribe (or equivalent) and breaking the column at the score. Inspect the cut through a magnifying glass to ensure that there are no jagged edges. The proper lengths of the column (to the base of the ferrule nuts) to be inserted into the injection and detection ports are 2.7 mm and 72 mm, respectively. Mark the placement of the nut with typewriter correction fluid on the column as a point of reference. Tighten the nuts.

New columns must be conditioned before method validation: Leave the column disconnected from the detection port. Ramp the oven temperature up to just below its maximum, at 1°C/min, and hold for 4 hours.

12.6 COLUMN RINSING

The GC column may be rinsed with several column volumes of appropriate solvents (both polar and non-polar). Depending on the nature of the sample residues expected, the first rinse could be water, followed by methanol and acetone. Methylene chloride is a good final rinse, and in some cases, may be the only solvent required. The column should then be filled with methylene chloride and stored overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen gas.

13.0 REFERENCES

- 13.1 EPA Method 8000B: Gas Chromatography.
- 13.2 EPA Method 8082: Polychlorinated Biphenyls (PCBs) by Capillary Column Gas Chromatography.
- 13.3 Great Lakes Analytical Quality Assurance Program.
- 13.4 Great Lakes Analytical Chemical Hygiene Plan.
- 13.5 Great Lakes Analytical SOP for Login Department.
- 13.6 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to the Great Lakes Analytical Quality Assurance Program Manual.

Figure 1.

Example Chromatogram for Aroclor 1016/1260 Mixture.

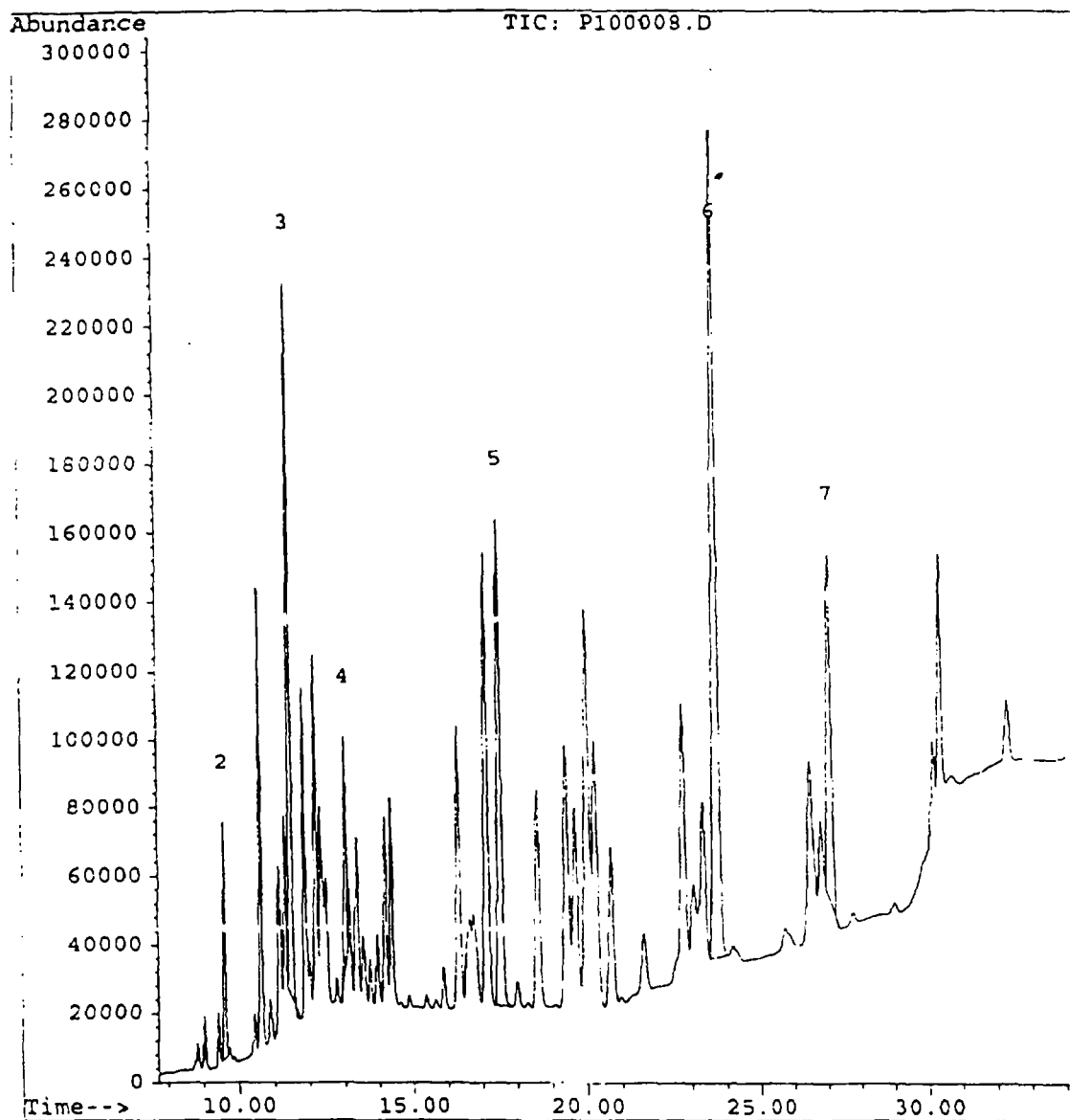
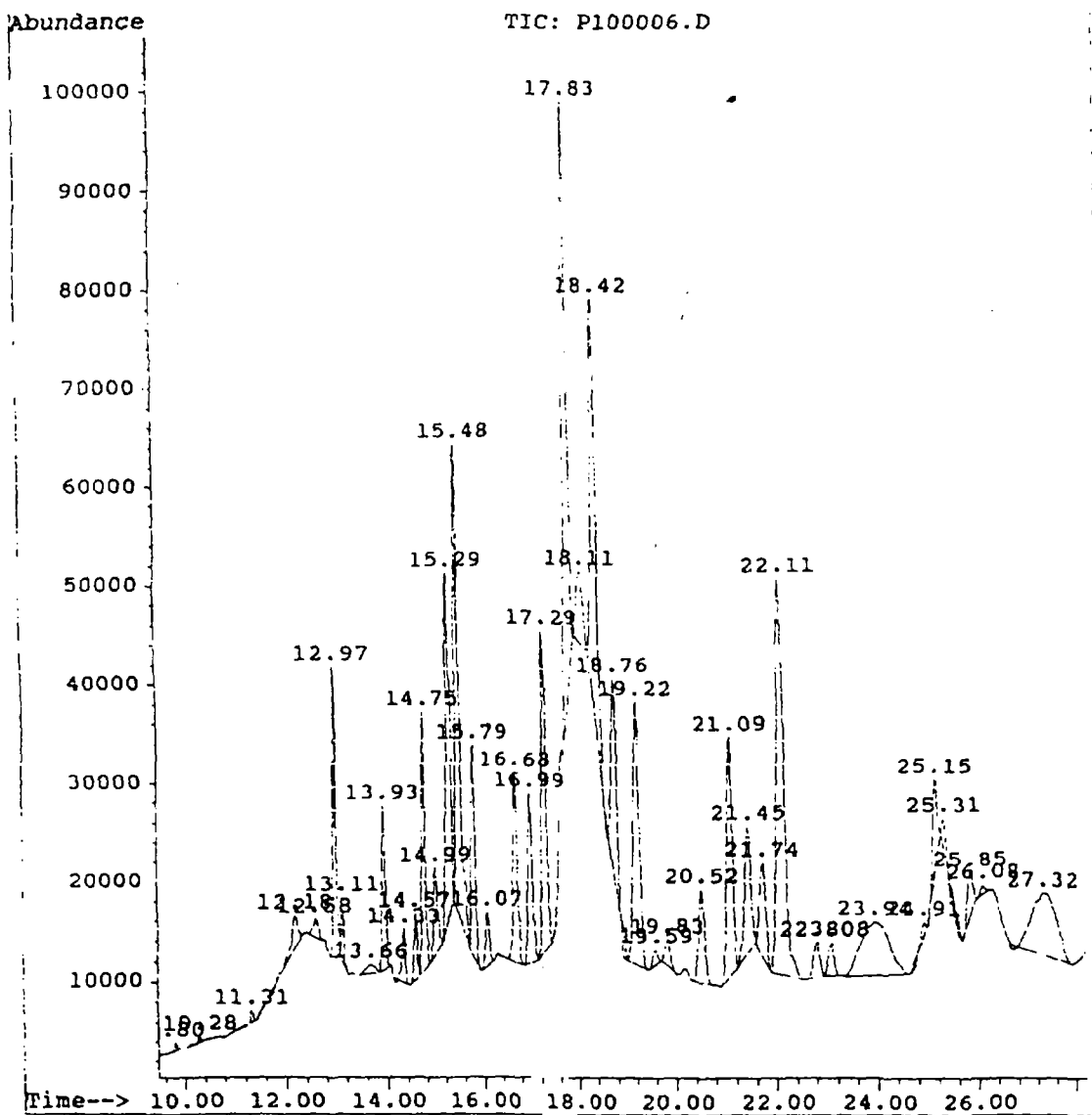


Figure 2.

Example Chromatogram for Aroclor 1254 Mixture.



DATA REVIEW

		YES	NO	CA	FLAG
1	Check standard recoveries within $\pm 15\%$?				
(8081) 1b	Prime and blank run?				
(8081) 1c	Endrine DDT breakdown < 15 % ?				
(8270) 1d	DFTPP tune evaluated and passing?				
(8270) 1e	SPCC average response factor > 0.050 ?				
(8270) 1f	CCC % deviation > 20 % ?				
(8270) 1g	Internal recoveries within 50-100 % ?				
2	Method blank recoveries < reporting limits?				
3	LCS within control limits?				
4	MS/MSD within control limits?				
5	All surrogate recoveries within control limits?				
6	All hits out of cal range diluted and re-analyzed?				
7	All sample holding times met?				
8	No transcription errors?				
9	No calculation errors?				

COMMENTS:

Analyst review signature: _____

Date: _____

**Method Detection Limits (MDL), Practical Quantitation Limits (PQL), and
Reporting Limits (RL)**

Method: PCBs by 8082

Analyte	Water (µg/L)			Soil (µg/Kg)		
	MDL	PQL	RL	MDL	PQL	RL
Aroclor 1016	0.0987	0.350	0.5	2.18	7.70	25
Aroclor 1260	0.0658	0.227	0.5	3.27	11.6	25
Aroclor 1221 (*)	0.10	NA	0.5	3.33	NA	25
Aroclor 1232 (*)	0.10	NA	0.5	3.33	NA	25
Aroclor 1242 (*)	0.10	NA	0.5	3.33	NA	25
Aroclor 1248 (*)	0.10	NA	0.5	3.33	NA	25
Aroclor 1254 (*)	0.10	NA	0.5	3.33	NA	25

(*)—This compound is a multi-component analyte. The MDL for this analyte is based on the lowest concentration at which pattern recognition can be performed.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS

BY PURGE-AND-TRAP AND

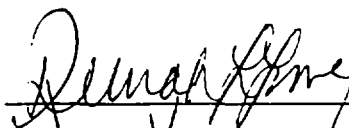
GAS CHROMATOGRAPHY/MASS SPECTROMETRY

GLA 8260 BG

Revision 2.1

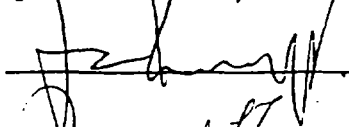
Approved By:

Department Manager:



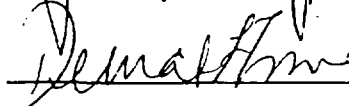
Date: 5/28/99

Quality Assurance Manager:



Date: 5/28/99

Laboratory Director:



Date: 5/28/99

1.0 APPLICABILITY

This procedure provides instructions for the analysis of samples for volatile organic compounds by a purge and trap extraction, followed by analysis with a gas chromatograph/mass spectrometer. This SOP is an interpretation of the SW-846 methods 8260B, 5030B, and 5035. It is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan, and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to water, soil, waste, and TCLP/SPLP matrices.

1.2 REGULATORY APPLICABILITY

40 CFR 121 (SW 846)

2.0 SUMMARY

This procedure describes the determination of volatile organic compounds by purge-and-trap, gas chromatography, and mass spectrometry. Helium is bubbled through a sample, purging out volatile components. These analytes are adsorbed onto a sorbent column (carbon trap). The trap is rapidly heated and backflushed with helium, desorbing the analytes onto a capillary column in a gas chromatograph. Once on the column, the analytes are separated by their interaction with the stationary phase of the column and the temperature program of the GC oven. The sample stream is reduced by a jet separator or a narrow bore restrictor column as it goes into the mass spectrometer. As analytes enter the detector, they are ionized by an ion source. Electrons fractionate the molecules, forming positive ions. Lenses focus the ion stream as it enters mass filtering quadrupoles. Varying AC and DC electronic signals on the quadrupoles permit ions with only certain mass to charge (m/z) ratios through the field. The filtered ion stream is then focused by another lens as it strikes the electron multiplier. The electron multiplier liberates neutralizing electrons that are proportional to ion abundance upon impact of the ion stream. The result is a total ion chromatogram as analytes are separated by the column with corresponding mass spectra in each peak. The peaks are identified by retention time and ion ratios. Each compound is assigned a primary characteristic ion. The area of this ion within its analytical peak is called an extracted ion current profile, or EICP of the characteristic ion. Quantitation is based upon generating response factors in a calibration study using EICP's for all compounds within the total ion chromatogram. Compounds which may be detected by this method are given in Appendix A.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves and safety glasses are worn when handling solvents, chemicals, and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 COMPRESSED GASES

All compressed gases, except air, can cause suffocation by displacing oxygen. Caution should be exercised when changing compressed gas cylinders. Analysts must wear safety glasses when changing cylinders or working with gas plumbing. All compressed gas cylinders must be secured at all times. A handtruck must be used to transport cylinders. The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place.

3.4 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.5 STANDARDS

The standards used for calibrations and quality control are known pollutants; therefore caution should be taken when handling them. Standard preparation should take place in a hood or well-ventilated area. Gloves will be worn when handling standards. Benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride are tentatively classified as known or suspected human or mammalian carcinogens, and should be handled accordingly.

4.0 INTERFERENCES

4.1 CONTAMINATION

Samples can become contaminated in the field or in transit. If trip and field blanks are analyzed with the sample group they can serve as a check for this type of contamination. A trip blank is a vial full of water that has accompanied the samples in transit. A field blank is a vial of reagent water that is poured through all the field equipment used in sampling. Contamination of samples can also occur during analysis from residue left by other samples in syringes, lines and glassware in the purge-and-trap, autosampler, column, or detector. A blank must be run through the analytical system every 12 hours to demonstrate that it is clean.

4.2 CARRYOVER

There are several ways residue, especially from a concentrated sample, can carryover into subsequent samples:

- 4.2.1 Trap carryover - All volatile components of a sample may not be sufficiently desorbed or baked off the trap, leaving residual hydrocarbons or specific analytes on the trap. These contaminants may come off the trap during the next run.
- 4.2.2 Glassware carryover - All volatile components may not be purged from the sample, leaving residual hydrocarbons or specific analytes in the glassware. These contaminants can be purged out with the next sample run in that position.

- 4.2.3 Line carryover - In a very concentrated sample, it is possible that the lines of the autosampler or purge-and-trap may become contaminated. This is evident when subsequent runs contain the same contaminant.
- 4.2.4 Column carryover - All of the hydrocarbons in a sample may not come off the column by the time the oven temperature program has finished. They elute as broad peaks in the next run.

If carryover is suspected for any reason, a blank should be run to verify a clean analytical system and any affected samples should be rerun. Individual autosampler positions should be baked out or have blanks run through them as necessary.

It is recommended that each purge-and-trap system have a "bake out" method that is performed before each analytical run. In this method, the line temperatures of the autosampler and the purge-and-trap are elevated and the autosampler positions are purged and baked without the addition of sample.

Syringe contamination and possible contamination from the extraction procedure are easily eliminated by rinsing syringes with water and spatulas with methanol between samples.

4.3 SAMPLE INTEGRITY

- 4.3.1 Samples submitted for volatiles analysis are kept at 4°C before analysis.
- 4.3.2 Water samples should be preserved with 1:1 hydrochloric acid in the field to pH<2 to kill any micro-organisms that may degrade the volatile aromatic compounds. Sample vials should be filled so that no headspace or air bubbles exist in the vial.
- 4.3.3 Soil samples are preserved based on the desired reporting limits. Low level soils are collected in containers that contain an aqueous solution of sodium bisulfate (1g of sodium bisulfate in 5ml water) as the preservative. High level soils are collected in containers which contain methanol as the preservative. Alternatively, soils may be collected in EnCore samplers, and sent to the lab for immediate transferring (within 48 hours of sampling) into vials with the appropriate preservative.

5.0 RECORD KEEPING

5.1 INSTRUMENT LOG

Each instrument has an Instrument Log. The instrument identification number and effective dates are written on the front cover. An instrument log is very helpful in tracking problems and is an important troubleshooting guide. Entries in this book include, but are not limited to:

- Installation of the instrument.
- Run parameters for the instrument, autosampler, and data system.
- Instrument and autosampler gas flows.
- All routine and unscheduled maintenance.

5.2 QUALITY CONTROL BOOK

A Quality Control Book is set up for each instrument. It has the instrument identification number on the outside cover. The contents of this book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP's and the source methods.

- Copies of the calibration studies and internal standard control limits and the dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Copies of all retention time studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Surrogate standard recovery tabulations and control limits.
- Corrective action sheets.

5.3 RUN LOG

On the front cover of the Run Log notebook display:

- Instrument identification number.
- Run log number.
- Effective dates.

The following column headings are written at the top of each page:

- Data file name.
- Date.
- Autosampler position.
- Client.
- Full sample number.
- Amount of sample analyzed with units.
- Method number.
- Results complete with units.
- Status of internal and surrogate standard recoveries.
- Comments.

Subsequent information for each sample and standard is then documented under the column headings. Additional documentation concerning standards includes:

- Quality control function (check standard, blank, matrix spike, etc.).
- Concentration.
- GLA code number.
- Recovery.

Each page is dated and signed. Laboratory notebooks must be neat and legible. Mistakes are crossed out with a single line, initialed, and dated. Unused or partial pages are z'd out.

5.4 SAMPLE SCHEDULE (LIMS)

Analysts keep track of sample throughput by using the LIMS (Laboratory Information Management System). The system is checked daily and all pertinent sample information is recorded, and a hard copy is generated. This information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time / turnaround time.

5.5 STANDARD PREPARATION LOG

When standards are received by the laboratory, the certificate of analysis is dated and placed in the Standards Preparation Certificate of Analysis binder. A log is kept of all the standards prepared for the volatiles methods. Document in this book:

- Analyte, Purpose (method, calibration, internal, etc.).
- Supplier.
- Lot number.
- Initial concentration of the stock solution.
- Volume diluted.
- Expiration date of stock standard - six months after the standard has been opened or the date set by manufacturer, whichever is first. Gas stock standards are good for one month after opened, or until the date set by the manufacturer, whichever is sooner.
- Final concentration.
- Volume prepared.
- Date prepared.
- Expiration date of working standard - three months after the standard has been made or when standard fails Quality Control criteria, whichever is first. Gas working standards expire after two weeks.
- GLA code for the final solution. The GLA code is a number and letter sequence used to track standard preparation within the department. It consists of the month number and successive letter of the alphabet starting with "A" at the beginning of each month.
- Initials.

5.6 BALANCE LOG

A balance log is kept to check the accuracy of the scale used in soil sample extractions. Entries are made on any day the scale is utilized. Record:

- Date.
- Weight of the Class P check weight less the tared weight.
- Scale reading.
- Weight of second Class P check weight less the tared weight.
- Scale reading.
- Initial each entry.

Any problems and corrective action taken should also be recorded in this log.

6.0 QUALITY CONTROL

6.1 BFB TUNE CHECK

- 6.1.1 4-Bromofluorobenzene (BFB) must be analyzed at the start of every 12 hour sequence. 1 μ l (50ng) of the working tuning solution is directly injected onto the GCMS system.
- 6.1.2 Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and is accomplished by using a single scan prior to the elution of BFB. Other techniques can be used as long as the apex is always included, and the other ions averaged are consecutive with the apex.

- 6.1.3 The key ions produced during the analysis of BFB and their respective ion abundance criteria are given below. This criteria must be met before any calibration standards, blanks, or samples can be analyzed.

<u>Mass</u>	<u>m/z abundance criteria</u>
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101% of mass 174
177	5 to 9% of 176

6.2 CALIBRATION VERIFICATION (CV)

The CV validates the initial calibration curve and is used to gauge the daily operating condition of the instrument. The CV (at 50 µg/L) is analyzed every 12 hours, after the 12 hour tune, but before actual samples are analyzed.

- 6.2.1 The minimum relative response factors (RRF's) of system performance check compounds (SPCC's) must meet method requirements:

<u>SPCC's</u>	<u>Min. RRF</u>
Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

$$RRF = \frac{EICP^* \text{ of analyte}}{\text{concentration of analyte}} \times \frac{\text{concentration of internal standard}}{EICP^* \text{ of internal standard}}$$

* of the characteristic ion

Note: When determining the RF, the internal standard used in the calculation is the one which elutes closest to the analyte.

- 6.2.2 Calibration check compounds (CCC's) must also meet specific criteria. The CCC's are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethyl benzene, vinyl chloride. For CCCs which are calculated by average response factor, the percent difference (%D) between the RF of the CCC compound and the corresponding average RF from the calibration curve must be $\leq 20\%$. For CCCs calculated by linear regression, the percent drift must be $\leq 20\%$. If the CCCs are not part of the target analyte list, then all target compounds must meet the 20% criteria.

$$\% \text{ Drift} = \frac{\text{known concentration} - \text{calculated concentration}}{\text{known concentration}} \times 100$$

The CCV can be used to check chromatography for peak shape. The check standard must fulfill the above criteria before samples can be analyzed.

6.3 METHOD BLANK

The method blank verifies that the analytical system is free from contamination.

- 6.3.1 The method blank is run every 12 hours, after the CV, but before samples are analyzed.
- 6.3.2 No contamination should be present in the blank above the reporting limit. If contamination is found, samples analyzed after the blank which contain the same contaminants must be reanalyzed to confirm the detects.
- 6.3.3 The method blank may be the field blank sample submitted by a client for a particular project.

6.4 INTERNAL STANDARD

Internal standards are added to everything analyzed by this method. Recoveries are a factor in the concentration calculations of analytes. They also monitor the efficiency of the purge-and-trap extraction procedure.

- 6.4.1 The internal standards are pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene- d_5 , and 1,4-dichlorobenzene- d_4 . The concentration of the internal standards is 50 ppb.
- 6.4.2 The retention times of the internal standards in the CVs must be within 30 seconds of retention times from the corresponding standard in the initial calibration.
- 6.4.3 The EICP areas of the characteristic ion of the internal standards in the CVs must be within 50% to 200% of those from the mid-point standard in the initial calibration.
- 6.4.4 When recoveries fall outside of the criteria, one sample from each effected project is re-analyzed to confirm a possible matrix effect. If the recoveries confirm, the data is reported from the original analysis and a corrective action form is filled out. If the recoveries of the internal standards fulfill criteria, the data from the re-analysis is reported.

6.5 SURROGATE STANDARDS

Surrogates are added to everything analyzed by this method. Surrogate standard recoveries are used to monitor the efficiency of the purge-and-trap extraction procedure.

- 6.5.1 The surrogate standards are dibromofluoromethane, 1,2-dichloroethene- d_4 , toluene- d_8 , and 4-bromofluorobenzene. The concentration of the surrogate standards is 50 $\mu\text{g/L}$.
- 6.5.2 The surrogate standard recoveries from 20 to 30 samples per matrix are tracked to determine the control limits. These limits are defined as the average recovery ± 3 times the standard deviation. Surrogate standard limits are kept in the QC binder and should be posted by the analyst for reference. Limits are determined annually.
- 6.5.3 When surrogate standard recoveries fall outside these limits, one sample from each effected project is re-analyzed to confirm a possible matrix effect. If the recoveries confirm, results are reported from the original analysis and a corrective action form is filled out. If the recoveries fulfill criteria, data from the re-analysis is reported.

6.6 MATRIX SPIKES

A set of matrix spike/matrix spike duplicates (MS/MSD) are analyzed regularly to check the effect of the sample matrix on the performance of the method.

- 6.6.1 An MS/MSD is analyzed per batch of 20 or less samples of the same matrix. Soil and water matrix spikes contain all of the analytes on the compound list at a concentration of 50 µg/L and 50 µg/Kg, water and soil respectively. TCLP spikes contain all of the analytes on the compound list at a concentration of 100 µg/L, except for 2-butanone, which is at 500 µg/L.
- 6.6.2 Spike recoveries for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 20 sets of MS/MSDs. These limits should be posted by the analyst for reference.

6.7 LABORATORY CONTROL SPIKE (LCS)

The results of the LCS are used to verify the laboratory can perform the analysis in a clean matrix (ie. when MS/MSDs results indicate potential problems due to the sample matrix).

- 6.7.1 An LCS is analyzed with each 12 hour analytical batch. Reagent water (for water LCS) or clean sand (for soil LCS) is spiked at 50ppb with the same solution and at the same concentration as the MS/MSD.
- 6.7.2 Spike recoveries for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 20 sets of MS/MSDs. These limits should be posted by the analyst for reference.

6.8 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented. Examples of when corrective sheets are filled out are:

- Check standard recovery fails for a particular compound that was present in the sample.
- Contamination was present in the blank and in the sample.
- Internal standard recovery is outside of 50-200% limits.
- Surrogate recovery is outside of control limits.
- Matrix spike recoveries are outside of control limits.

6.9 CHECKLISTS

Checklists are designed to ensure that data being reported by the laboratory has met all of the daily quality control requirements. The analyst documents the status of all quality control requirements for an analytical batch by checking off and filling out Daily Batch Checklists prior to reporting results. If quality control criteria has failed, the analyst must document samples that were affected and whether or not corrective action was taken. (Please see attached checklists.)

7.0 SAMPLE MANAGEMENT

- 7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 HOLD TIME

- 7.2.1 Water samples preserved to a pH of less than 2 have a hold time of 14 days from the date sampled. Unpreserved water samples have a hold time of 7 days from the date sampled.
- 7.2.2 Soil samples received by the laboratory preserved with sodium bisulfate or methanol (see section 4.3) have a hold time of 14 days from the date sampled. Soil samples submitted to the lab in EnCore samplers, or in jars, must be preserved within 48 hours of sampling. Then, a holdtime of 14 days from the date of preservation is in effect.
- 7.2.3 Soil samples submitted for TCLP analysis must be zero headspace extracted within 14 days of sampling. An additional 14 day holdtime is in effect after the TCLP extraction has been performed.
- 7.2.4 If a sample is received or analyzed past the holdtime, the client is immediately informed of the problem, and the report is qualified.

7.3 SAMPLE SCHEDULE

Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for method 8260 are queued under "VOMS". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

7.4 DISPOSAL

The analyst disposes of extracted samples one week after the date of analysis. Methanol and remaining fluid in the purge tubes is placed in the solvent drum. The login department maintains the other volatiles refrigerators. TCLP/SPLP extracts are disposed of one week after analysis. The extract is poured into the acid waste drum.

7.5 HAZARDOUS SAMPLES

If upon sample analysis analytes with concentrations above "Red Tag Limits" are found, the login department is notified by filling out a red tag sheet, and red tape is placed on the sample container. (See the GLA SOP for Hazardous Sample Management.)

RED TAG LIMITS

<u>Compound</u>	<u>mg/kg</u>	<u>mg/L</u>
Benzene	8	0.4
Carbon tetrachloride	8	0.4
Chlorobenzene	1600	80
Chloroform	96	4.8
1,2-Dichloroethane	8	0.4
1,1-Dichloroethene	11	0.56
Methyl ethyl ketone	3200	160
Tetrachloroethene	11	0.56
Trichloroethene	8	0.4
Vinyl chloride	3.2	0.16

8.0 METHOD VALIDATION

8.1 INITIAL CALIBRATION STUDY

An initial calibration study determines the average response factors for the target and surrogate analytes that in turn are used to quantitate the concentration of these compounds in a sample. An internal standard calibration technique is employed in which the same concentration of internal standard is added to a series of freshly prepared calibration standards which encompass the linear range of the detector. The initial calibration must be developed before samples, blanks, and QC samples can be analyzed.

- 8.1.1 A minimum of five calibration levels are prepared and analyzed. For soil analysis, the calibration points are 5, 50, 100, 150, 200, and 250 µg/L. For water samples, the calibration points are 2, 10, 50, 100, 150, 200, and 250 µg/L. All target analytes, including surrogates, must be included in the each calibration level. Internal standards (at 50 ppb) are also added to each calibration level.
- 8.1.2 The RRFs are calculated (see 6.2.1) for each target analyte and surrogate in each calibration level. The average RRF is then calculated for all analytes, using all of the levels in the calibration study.
- 8.1.3 The average RRF's for the SPCCs must meet the minimum RRF requirements specified in section 6.2.1.
- 8.1.4 The percent relative standard deviation (%RSD) is calculated for all the analytes:

$$\%RSD = \frac{\text{standard deviation}}{\text{average RF}} \times 100$$

- 8.1.5 The %RSD for the CCCs (section 6.2.2) must be $\leq 30\%$.
- 8.1.6 If the %RSD is $\leq 15\%$ for all included analytes, then the calibration is considered linear, and the average RRF is used for quantitating samples, blanks, and QC. However, if the %RSD exceeds 15%, a least squares linear regression curve must be created for each analyte above the 15%.

$$y = mx + b \quad \begin{array}{l} \text{where } y = \text{EICP area for the analyte} \\ m = \text{Slope of the curve} \\ x = \text{Concentration of the calibration standard} \\ b = \text{The } y \text{ intercept of the curve} \end{array}$$

Note: The correlation coefficient generated by the regression must be ≥ 0.99 in order for it to be used for quantitation purposes.

- 8.1.7 If any of the above criteria is not met for the calibration, corrective action is performed, and another calibration study is analyzed.

8.2 DETECTION LIMIT STUDY

This study is performed in accordance with the GLA Quality Assurance Program. This study provides the analyst with the method detection limit (MDL) for the instrument and analytes. The MDL is defined as the minimum concentration of the analyte that can be measured and reported with 99% confidence. The MDL is equal to the standard deviation of the recoveries of seven aliquots multiplied by the analysts' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The analysts' t value appropriate for 7 aliquots is 3.143. The calculated MDL

must be between 100% and 10% of the concentration of the MDL standard in order to be valid. An MDL study is done yearly per matrix.

- Run 7 replicate low level standards (at or below lowest calibration level standard).
- $MDL = \text{standard deviation} \times 3.143$.
- The calculated MDL must be less than reporting limit.

8.3 ACCURACY AND PRECISION STUDY

To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operation:

- Run 4 replicate standards at 50 µg/L.
- Recoveries of all compounds must be between 80-120%.
- The relative standard deviation must be less than 20%.

The study is performed by each analyst in charge of a new method, or when major maintenance is performed (changing a column, changing oven parameters).

9.0 EQUIPMENT

9.1 System 1 -

Purge-and-trap system:

- Tekmar LSC 2000 sample concentrator.
- Tekmar Archon autosampler.
- Supelco VOCARB 3000 trap - 10 cm Carboxen 1001.

Operating parameters:

- Purge pressure: 20 psi.
- Purge flow: 40 mL/min.
- Purge time: 11 min.
- Desorb time: 4 min. at 240°C
- Bake: 10 min. at 260°C

Hewlett Packard 5890 Gas Chromatograph equipped with a Restek RTX-502.2 0.53 mm ID X 60 m column, Jet Separator interface and Hewlett Packard 5971 MSD. (GC/MS-1, Installed 7/91.)

Oven parameters:

- Mass spectrometer interface (Detector B) temperature: 250°C.
- Jet separator temperature (Detector A): 200°C.
- Injector temperature: 250°C.
- Temperature program: 36°C for 10 minutes increase 8°C/min. to 210°C, hold for 1 min.

Linear velocity of helium at 150°C: 59 cm/sec.

Column head pressure at 35°C: 6 psi.

Hewlett Packard Chemstation and Enviroquant Data Management System.

9.2 System 2 (for low level soils)-

Purge-and-trap system:

- Tekmar LSC 3000 sample concentrator.
- Tekmar 2016 Purge and Trap Autosampler.
- Supelco VOCARB 3000 trap - 10 cm Carboxen 1001.

Operating parameters:

- Purge pressure: 20 psi.
- Purge flow: 40 mL/min.

- Purge time: 11 min.
- Desorb time: 4 min. at 240°C
- Bake : 10 min. at 260°C

Hewlett Packard 5890 Gas Chromatograph equipped with a J&W DB 624 0.53 mm ID X 75 m column, narrow-bore restrictor column interface, and Hewlett Packard 5972 MSD. (GC/MS-3, installed 10/94.)

Oven parameters:

- Mass spectrometer interface (Detector B) temperature: 250°C.
- Injector temperature: 250°C.
- Temperature program: 40°C for 10 minutes increase 8°C/min to 220°C hold for 3 min.

Linear velocity of helium at 110°C: 37 cm/sec.

Column head pressure at 35°C: 8 psi

Hewlett Packard Chemstation and Enviroquant Data Management System.

9.3 Mass Spectrometer Parameters

Scan range : 35 to 400 amu

Scan Rate : 2.08scans/second

Specific instrument parameters can be found in the instrument maintenance log.

10.0 STANDARDS AND REAGENTS

10.1 STANDARD SOURCES

Standards are ordered from EPA or A2LA Certified companies. These companies include Accustandard, Restek, Supelco, and Ultra Scientific.

10.2 STANDARD DILUTIONS

Standards are volatile so special care should be taken to preserve their integrity. Stock and working standards are kept in a freezer between -10 and -20°C when not in use.

A useful equation for standard preparation is:

$$C_1V_1 = C_2V_2$$

Where:

C_1 is the initial concentration of the stock standard.

C_2 is the desired concentration of the working standard.

V_2 is the volume of working standard to be prepared.

V_1 is the volume of stock standard to be diluted.

10.3 STOCK STANDARD

Transfer stock standard to a vial and seal with Teflon-lined cap. Label this vial with:

Analyte description.

Manufacturer.

Lot number.

Concentration.

Date opened.

Expiration date.

Store in a freezer. The stock standard expires six months after it is opened or the expiration date set by the manufacturer, whichever is first. Opening of the standard is documented in the Volatile Standard Log.

10.4 WORKING STANDARD

Standards are diluted in methanol:

- Fill a volumetric flask about three quarters of the way full with methanol.
- Add desired amount of stock standard.
- Fill volumetric flask to meniscus.
- Cap and invert three times.
- Transfer to vial with "mini-nert" cap.
- Label vial with:
 - Analyte description.
 - Concentration of standard.
 - Date made.
 - Purpose.
 - Initials.
 - Expiration date.
 - GLA code.

The working standard expires three months after it is opened or when the standard fails Quality Control Criteria, whichever is first. Preparation is documented in the Volatile Standard Log.

10.5 REAGENTS

- 10.5.1 Methanol - Purge-and-trap grade methanol is used for extractions and standard preparation.
- 10.5.2 Reagent water - Bottled drinking water is boiled for three minutes and then purge with nitrogen before use in analyses.
- 10.5.3 Gases - Ultra-high purity grade helium.

11.0 PROCEDURE

- 11.1 Before samples can be prepared for loading onto the instrument, all utensils must be cleaned. Syringes used for fortifying samples are rinsed several times with purge and trap grade methanol. 5ml syringes are rinsed several times with reagent grade methanol and twice with reagent water. Purge vessels are also rinsed several times with reagent grade methanol, and twice with reagent water.
- 11.2 Before anything can be loaded and analyzed, the purge and trap autosampler must be cleaned. This involves flushing the sample valves and sparger needles with several mls of a 1:1 water/methanol mix. A plastic 25ml syringe is twisted onto the sample valve, the valve is opened, and several mls of the mix is injected through the valve and collected at the end of the sparger needle with a 500 ml plastic beaker. The sparger needle is wiped clean with a kimwipe. This process is repeated for each autosampler port.
- 11.3 If highly concentrated samples (eg. exceed the calibration range) have been analyzed on the instrument (on column concentrations > 400 ppb), a bake-out procedure is required. This involves purging each port for 2 minutes and heating each sample line to 180 °C. Consult instrument maintenance procedures for complete details.

11.4 A typical analytical run would be as follows:

BFB Tune	}	Analyze calibration curve as needed
Calibration Std #1		
Calibration Std #2		
Calibration Std #3		
Calibration Std #4		
Calibration Std #5		
CV		
Method Blank		
QC Check Sample		
Sample Analysis (# of samples dependent on 12 hour clock)		
MS (per 20 samples or less by matrix)		
MSD (per 20 samples or less by matrix)		

- 11.5 All of the following procedures and the order of analysis must be documented in the Volatiles Run Logbook.
- 11.6 Before analyzing calibration standards, CVs, blanks, QC, and samples, a BFB tune is analyzed by injecting the appropriate amount of the working BFB tune solution (50 ng on-column). All the criteria in Section 6.1.3 must be met before proceeding with the typical run outlined above.
- 11.7 After an acceptable BFB tune has been analyzed, an initial calibration is prepared and analyzed. A minimum of five calibration standards are prepared in 5 ml of reagent water (in 5ml sodium bisulfate preservative solution for low level soils using the Archon autosampler), and analyzed from low (5ppb) to high (400ppb) concentration. All the criteria in Section 8.1 must be met before samples can be analyzed.
- 11.8 Once an initial calibration is established, a CV is prepared (@50ppb) in 5 ml of reagent water (in 5ml sodium bisulfate preservative solution for low level soils using the Archon autosampler) and analyzed. All the criteria in Section 6.2 must be met before samples can be analyzed.
- 11.9 Next, a method blank is prepared in 5 ml reagent water (5ml sodium bisulfate preservative solution for Archon autosampler) by fortifying the water with internal standard and surrogate only (@ 50ppb). The analytical results must fulfill Section 6.3 before samples can be analyzed.
- 11.10 Finally, an LCS is prepared (@50ppb) in 5 ml reagent water (5ml sodium bisulfate preservative solution with ~ 5.0g clean sand for Archon autosampler), or 5g of clean sand (med/high level soils), and analyzed. The recovery limits described in Section 6.7 should be fulfilled.
- 11.11 Once 11.6 through 11.10 have been completed, samples can be analyzed.

11.2 Water Sample Analysis

- 11.2.1 All samples are removed from the volatiles storage refrigerator and allowed to reach room temperature.
- 11.2.2 Water samples are prepared in 5ml syringes. The plunger is removed from the syringe and the syringe barrel is filled with the sample.
- 11.2.3 The plunger is placed into the barrel, and the volume is adjusted to 5ml, taking care of eliminating any air bubbles in the syringe.
- 11.2.4 The appropriate amount of internal standard/surrogate is added (50ppb), and the sample is loaded onto the instrument.

- 11.2.5 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is also added to each syringe.
- 11.2.6 All compounds must fall within the established calibration range. Dilutions of water samples are prepared in 5ml syringes. Dilutions should be made to get the majority of the target compounds within the upper half of the calibration. Aliquots of the sample are added to reagent water to obtain a final volume of 5ml. For high level water samples, volumetric flasks are used to make serial dilutions before diluting to a final volume of 5ml.
- 11.2.7 After a water sample has been loaded, the pH of the sample is taken by dipping a pH strip into the opened sample vial. The pH is recorded in the Volatiles Run Logbook.

11.3 TCLP/SPLP Sample Analysis

- 11.3.1 After the samples are leached by the zero headspace technique, samples are given to the Volatiles group for analysis.
- 11.3.2 Leached samples are prepared in 5ml syringes. The plunger is removed from the syringe and the syringe barrel is filled with reagent water.
- 11.3.3 The plunger is placed into the barrel, and the volume is adjusted to 4.75ml, taking care of eliminating any air bubbles in the syringe.
- 11.3.4 Then, 250µl of the leached sample is added to the syringe.
- 11.3.5 The appropriate amount of internal standard/surrogate is added (50ppb), and the sample is loaded onto the instrument.
- 11.3.6 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is also added to each syringe.
- 11.3.7 All compounds must fall within the established calibration range. Dilutions of water samples are prepared in 5ml syringes. Dilutions should be made to get the majority of the target compounds within the upper half of the calibration. Aliquots of the sample are added to reagent water to obtain a final volume of 5ml. For high level water samples, volumetric flasks are used to make serial dilutions before diluting to a final volume of 5ml.

11.4 Low Level Soil Analysis

This procedure is used for samples preserved with sodium bisulfate. Estimated concentrations for this procedure are projected to be < 200 µg/Kg.

- 11.4.1 The exact amount of soil in each vial is determined and documented in the Volatiles Extraction Logbook. The weight is determined by subtracting the weight of the vial containing the preservative and stir bar from the vial containing the preservative, stir bar, and soil.
- 11.4.2 All samples are removed from the volatiles storage refrigerator, and allowed to reach room temperature.
- 11.4.3 The sample vials, containing ~5.0g of soil, 5ml of the sodium bisulfate preservation solution, and a stir bar, are gently shaken to insure free flowing of the sample for stirring. Vials are then placed into the Archon autosampler.

- 11.5.8 All sample results must fall within the established calibration range. Dilutions should be made to get the majority of the target compounds within the upper half of the calibration. Samples are diluted further by varying the amount of extract added to the purge water. The amount of extract added must be $\geq 10\mu\text{l}$ and $\leq 100\mu\text{l}$. For larger dilutions, serial dilutions of the extract are performed using volumetric flasks.

11.6 General Analysis Notes

- 11.6.1 Each analytical batch must be completed within a 12 hour time frame. Any analysis performed outside the 12 hour clock must be reanalyzed. The twelve hour clock starts at the time of the BFB tune.
- 11.6.2 All compounds must fall within the established calibration range, unless the client allows sample results to exceed the calibration range. Reported results which exceed the calibration range are flagged as estimated.
- 11.6.3 If exceedance of the calibration range is allowed, reanalysis is still required if the exceeding result is below the requested reporting limit.
- 11.6.4 If a sample is analyzed immediately following a highly concentrated sample, reanalysis of the sample should be considered.
- 11.6.5 If a highly concentrated sample (>400 ppb for any target compound) is analyzed on a port, instrument blanks must be analyzed in that port until analytical results show no detection above the reporting limit. An instrument blank is prepared the same as a method blank.

11.7 Qualitative Analysis

- 11.7.1 Qualitative identification of compounds is based on relative retention time (RRT) and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. Appendix A lists the characteristic ions for all the target compounds.
- 11.7.2 The RRT of the suspected constituent in the sample must be within ± 0.06 RRT units of the RRT of the standard compound.
- 11.7.3 The intensities of the characteristic ions of a compound should maximize in the same scan, or within one scan of each other. This is determined automatically with the data systems target compound search routine.
- 11.7.4 The relative intensities of the characteristic ions should agree within 30% of the relative intensities of these ions in the reference spectrum (ex. For an ion abundance of 50% in the reference spectrum, the corresponding abundance in the sample spectrum can range between 20% and 80%).
- 11.7.5 For those isomer compounds that produce very similar mass spectra, the retention time should be used to identify the individual isomers.
- 11.7.6 If a compound cannot be verified by the above criteria, but in the technical judgement of the analyst, the identification is correct, then the compound shall be reported.

11.8 Quantitative Analysis

- 11.8.1 After a compound has been qualitatively identified following Section 11.18, the concentration of a target compound can be calculated based on the EICP area of the compound. Integration of EICP of the characteristic ion is performed automatically by the data system.

- 11.8.2 Manual integrations done specifically to meet method or contract quality control requirements are not permitted. There are situations when manual integration may be necessary, such as complex samples where partial coelution of peaks occur, or when the baseline has not been assigned adequately by the data system. In the instances, the trained analyst shall use their best technical judgement in the integration of the chromatogram.
- 11.8.3 The internal standard technique is used for quantitation (see Section 8.1). If the RSD from the calibration for a compound is $\leq 15\%$, then the AvgRRF maybe used in the calculation of the concentration. If the RSD from the calibration for a compound is $>15\%$, then the linear regression is used to calculate the concentration.

12.0 CALCULATIONS

12.1 Water Samples (using AvgRRF)

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_x)(I_s)(DF)}{(A_s)(\text{AvgRRF})(V_o)}$$

where:

A_x = Area of the characteristic ion of the compound

A_s = Area of the characteristic ion of the internal standard

I_s = IS amount in nanograms (ng)

AvgRRF =Average relative response factor from the calibration

V_o = Final volume of water purged in ml's (5ml)

DF =Dilution factor. The dilution factor for analysis of water samples for volatiles by this method is defined as the ration of the number of milliliters (mL) of water purged (i.e. V_o above) to the number of mL of the original water sample used for purging. For example, for TCLP samples, 0.25ml of sample is diluted to 5.0 mL with reagent water and purged -- $DF=5.0\text{mL}/0.25\text{mL} = 20$. If no dilution is performed, $Df = 1.0$.

12.2 Low Level Soils (Using AvgRRF)

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_x)(I_s)}{(A_s)(\text{AvgRRF})(V_o)}$$

where:

A_x = Area of the characteristic ion of the compound

A_s = Area of the characteristic ion of the internal standard

I_s = IS amount in nanograms (ng)

AvgRRF =Average relative response factor from the calibration

V_o = Final weight of soil purged in grams

12.3 Soil/Sediment/Waste Samples (using AvgRRF)

$$\text{Concentration } (\mu\text{g/Kg}) = \frac{(A_x)(I_s)(V_i)}{(A_s)(\text{AvgRRF})(V_i)(W_s)(D)}$$

where:

A_x , A_s , I_s and AvgRRF are the same as for the water calculation above

V_i = For Med/High level samples: Volume of total extract (μl)

V_i = For Med/High level samples: Volume of extract added for purging (μl)

W_s = Weight of sample extracted or purged (g)

D = % dry weight, where $D = (100 - \% \text{moisture})/100$

- 12.4 Sample Quantitation by Linear Regression: Samples which require quantitation from a linear regression calibration curve will follow the following general equation:

$$C = (m(A) + b) \times DF$$

where:

C = Concentration of the compound

m = Slope of the calibration curve

A = Ratio of the sample EICP area to the internal standard EICP area

b = Intercept of the calibration curve (based on order of regression used)

DF = Dilution factor (based on 5ml, 25ml, or 5g of sample purged)

- 12.5 Surrogate Percent Recovery

$$\% \text{ Recovery} = \frac{\text{concentration found}}{\text{concentration spiked}} \times 100$$

- 12.6 Matrix Spike Recovery

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = spiked sample result

SR = sample result

SA = spike added

- 12.7 Relative Percent Difference (RPD)

$$RPD = \frac{|(MSR - MSDR)|}{(1/2)(MSR + MSDR)} \times 100\%$$

where:

MSR = matrix spike recovery

MSDR = matrix spike duplicate recover

13.0 REPORTING NOTES

- 13.1 Data is reported in $\mu\text{g}/\text{kg}$ or $\mu\text{g}/\text{L}$. This is equal to parts per billion, or ppb.

$$\frac{\mu\text{g}}{\text{kg}} = \frac{\mu\text{g}}{\text{kg}} \times \frac{1000 \text{ ng}/\mu\text{g}}{1000 \text{ g}/\text{kg}} = \frac{\text{ng}}{\text{g}}$$

$$\frac{\mu\text{g}}{\text{L}} = \frac{\mu\text{g}}{\text{L}} \times \frac{1000 \text{ ng}/\mu\text{g}}{1000 \text{ mL}/\text{L}} = \frac{\text{ng}}{\text{mL}}$$

- 13.2 If an analyte is not present or present below the reporting limit (RL), report the result as N.D. or "non-detected". However, upon request, analytes detected above the method detection limit (MDL) but below the RL are reported as estimated.

- 13.3 If a sample is analyzed with dilution, a dilution factor needs to be applied to the reporting limit. Reporting limits are based on full strength sample aliquots of 5.0g for soils, 5.0ml for waters, and 250 μl for TCLP extracts.

$$\text{Dilution factor (DF)} = \frac{\text{full strength}}{\text{amount analyzed}}$$

$$\text{Raised reporting limit} = \text{reporting limit} \times DF$$

14.0 LIBRARY SEARCH

- 14.1 Tentatively Identified Compounds (TICs): To identify compounds which are not part of the targeted and calibrated list, a library search is performed on the mass spectra to determine tentative identification.
- 14.2 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.
- 14.3 The relative intensities of the major ions should agree within $\pm 20\%$ (ex. For an ion abundance of 50% in the standard spectrum, the corresponding abundance in the sample spectrum can range between 30% and 70%).
- 14.4 Molecular ions present in the reference spectrum should be present in the sample spectrum.
- 14.5 Ions present in the sample spectrum but not in the reference spectrum are reviewed for possible background contamination or coelution of another compound.
- 14.6 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible background subtraction by the data system.
- 14.7 If in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound shall be reported as unknown. Additional classification shall be made if possible (i.e. Unknown hydrocarbon).
- 14.8 The 10 largest non-target peaks on the chromatogram are quantitated against the closest eluting internal standard. The RF for each unknown compound is assumed to be one.

15.0 INSTRUMENT MAINTENANCE LOG

- 15.1 It is very important to maintain an accurate and detailed instrument maintenance log. Document all problems and attempts at correcting them as well as results. This information is invaluable when the problem recurs and a clear solution is laid out. Documentation of routine maintenance such as changing tanks and cleaning the detector can also provide insight into a subsequent problem.

16.0 TROUBLESHOOTING

- 16.1 When troubleshooting the system for a chromatography or sensitivity problems it is important to isolate the problem. Only change one thing at a time. A standard should be run after every change to see if any progress has been made. The instrument maintenance log should have all run parameters documented. Check these parameters to see if they have changed.
- 16.2 Direct Inject: A direct injection bypasses the purge-and-trap system. If the direct injection looks bad, the problem is with the gas chromatograph or the detector. If the direct inject looks good, then the problem probably is with the purge-and-trap system.
- 16.3 Checking flows: Attach flow meter to vent on the sample concentrator. Step to purge. Measure flow in ml/min. by using timer on GC.
- 16.4 Checking for leaks: Use the Gowmac leak detector at all unions in the injection port, in the detector, at the regulators on the GC or use methanol to see if it bubbles. To leak check the purge-and-trap, cap off the vent on the sample concentrator. Step the unit to purge. The sparge vessel should stop bubbling at about 7 minutes. If the instrument stops bubbling before 6 minutes there is a leak in gas lines before the sparge vessel. If the instrument

continues to bubble past 8 minutes there is a leak in the gas lines after the sparge vessel. The MSD can be set up to look for the mass of methanol. Enter the mass of methanol (31) into the scan parameters and squirt methanol around any unions. If there is leak the methanol mass peak will get larger as the methanol reaches the detector.

- 16.5 Column installation: Column re-installation is necessary whenever maintenance is done to the injection or detection ports. A new column is necessary when there is an elevated baseline or the chromatography is bad. To install a column, slide the appropriate nuts and ferrules over the ends of the column. Cut 15 cm off both ends of the column by scoring the coating with a sapphire scribe (or equivalent) and breaking the column at the score. Inspect the cut through a magnifying glass to insure that there are no jagged edges. Consult the instrument manual for the proper length of the column to be inserted into the injection or detection ports. Mark the placement of the nut with typewriter correction fluid on the column as a point of reference. If the column is new, it must be conditioned before it is ready for method validation. Leave the column disconnected from the detection port. Ramp the oven temperature up at 1°C/min. to just below its maximum and hold for 4 hours.

16.6 Other sources of problems

- 16.6.1 Trap - Indications of a bad trap are: benzene in the blank, decreased internal area, back-pressure in the autosampler, decreased carbon tetrachloride response.
- 16.6.2 Standards - Bad standards are easily detected by analyzing them on multiple I instruments.
- 16.6.3 Glassware - Indication of glassware or autosampler position problems include poor check standard or spike recoveries repeatedly in one position, poor surrogate and internal standard recoveries always in the same position.
- 16.6.4 Injection port - Due to the direct injections of BFB, it is often necessary to change the septa in the injection port so that there is not a leak.
- 16.6.5 Dirty detector - Indications of a dirty detector include: BFB will not pass specification; Low high mass abundance; High background; High EM voltage

17.0 REFERENCES

- 17.1 SW-846 Method 5030B: Purge-and-Trap for Aqueous Samples.
- 17.2 SW-846 Method 5035: Closed-System Purge-and-Trap and Extraction Volatile Organics in Soil and Waste Samples.
- 17.3 SW-846 Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry.
- 17.4 Great Lakes Analytical Quality Assurance Program Manual.
- 17.5 Great Lakes Analytical Chemical Hygiene Plan.
- 17.6 Great Lakes Analytical SOP for Login Department.
- 17.7 Great Lakes Analytical SOP for Hazardous Sample Management.

APPENDIX A.

DETECTABLE COMPOUNDS.

	Primary Characteristic <u>Ion</u>		Primary Characteristic <u>Ion</u>
Acetone ^{a,b}	58	1,3-Dichloropropane	76
Acrolein	56	2,2-Dichloropropane	77
Acrylonitrile	53	1,1-Dichloropropene	75
Benzene ^{a,b}	78	cis-1,3-Dichloropropene ^a	75
Bromobenzene	156	trans-1,3-Dichloropropene ^a	75
Bromochloromethane	128	Diisopropyl ether	45
Bromodichloromethane ^a	83	Ethyl benzene ^{a,b}	91
Bromoform ^a	173	2-Hexanone ^a	43
Bromomethane ^a	94	Hexachlorobutadiene	225
2-Butanone (MEK) ^{a,b}	72	Isopropyl benzene	105
n-Butylbenzene	91	p-Isopropyltoluene	119
sec-Butylbenzene	105	4-Methyl-2-pentanone (MIBK) ^{a,b}	100
tert-Butylbenzene	119	Methylene chloride ^{a,b}	84
Carbon disulfide ^{a,b}	76	Methyl tert-butyl ether	73
Carbon tetrachloride ^{a,b}	117	2-Nitropropane ^b	46
Chlorobenzene ^{a,b}	112	Naphthalene	128
Chlorodibromomethane ^a	129	n-Propylbenzene	91
Chloroethane ^a	64	Styrene ^a	104
2-Chloroethylvinyl ether ^a	63	1,1,1,2-Tetrachloroethane	131
Chloroform ^a	83	1,1,2,2-Tetrachloroethane ^a	83
Chloromethane ^a	50	Tetrachloroethene ^{a,b}	164
2-Chlorotoluene	91	Tetrahydrofuran	42
4-Chlorotoluene	91	Toluene ^{a,b}	92
1,2-Dibromo-3-chloropropane	75	1,2,3-Trichlorobenzene	180
1,2-Dibromoethane	107	1,2,4-Trichlorobenzene	180
Dibromomethane	93	1,1,1-Trichloroethane ^{a,b}	97
1,2-Dichlorobenzene	146	1,1,2-Trichloroethane ^{a,b}	83
1,3-Dichlorobenzene	146	Trichloroethene ^{a,b}	95
1,4-Dichlorobenzene	146	Trichlorofluoromethane ^{a,b}	151
Dichlorodifluoromethane	65	1,1,2-Trichloro-1,2,2-trifluoroethane ^b	101
1,1-Dichloroethane ^a	63	1,2,3-Trichloropropane	75
1,2-Dichloroethane ^a	62	1,2,4-Trimethylbenzene	105
1,1-Dichloroethene ^a	96	1,3,5-Trimethylbenzene	105
cis-1,2-Dichloroethene ^a	96	Vinyl acetate ^a	43
trans-1,2-Dichloroethene ^a	96	Vinyl chloride ^a	62
1,2-Dichloropropane ^a	63	m,p,o-Xylenes ^{a,b}	106
		Methyl iodide	142
Internal standards:		Surrogate standards:	
Pentafluorobenzene	168	Dibromofluoromethane	113
1,4-Difluorobenzene	114	1,2-Dichloroethane-d ₄	65
Chlorobenzene-d ₅	117	Toluene-d ₈	98
1,4-Dichlorobenzene-d ₄	152	4-Bromofluorobenzene	95

^a Priority Pollutant Compounds^b F-list Compound

**Method Detection Limits (MDL), Practical Quantitation Limits (PQL), and
Reporting Limits (RL)**
Method: Volatiles by 8260

Analyte	Ret Times (minutes)	Water (µg/L)			Soil (µg/Kg)		
		MDL	PQL	RL	MDL	PQL	RL
Acetone	5.39	3.93	12.51	10	9.46	30.13	10
Benzene	12.85	1.05	3.36	2	0.72	2.31	5
Bromobenzene	22.98	1.06	3.38	2	0.64	2.02	5
Bromochloromethane	11.09	0.88	2.79	2	0.66	2.10	5
Bromodichloromethane	16	0.97	3.10	2	0.85	2.71	5
Bromoform	22.12	1.13	3.59	2	0.73	2.32	5
Bromomethane	3.56	0.69	2.20	2	0.88	2.80	5
2-Butanone	10.64	5.86	18.66	10	3.65	11.64	10
n-Butylbenzene	25.55	0.75	2.38	2	0.65	2.08	5
sec-Butylbenzene	24.5	0.36	1.14	2	0.65	2.07	5
tert-Butylbenzene	27.08	0.44	1.41	2	0.73	2.33	5
Carbon Disulfide	5.44	2.49	7.92	2	1.54	4.91	5
Carbon Tetrachloride	12.08	1.05	3.35	2	1.06	3.36	5
Chlorobenzene	20.49	0.80	2.54	2	0.76	2.43	5
Chloroethane	3.74	1.09	3.47	2	0.98	3.12	5
Chloroform	11.41	1.18	3.76	2	1.00	3.17	5
Chloromethane	2.87	1.01	3.23	2	1.04	3.31	5
2-Chlorotoluene	23.33	0.96	3.04	2	0.82	2.63	5
4-Chlorotoluene	23.57	1.13	3.59	2	0.51	1.63	5
Dibromochloromethane	19.35	0.84	2.68	2	0.74	2.34	5
1,2-Dibromo-3-chloropropane	27.16	1.64	5.24	2	1.13	3.59	5
1,2-Dibromoethane	19.56	0.79	2.51	2	0.66	2.11	5
Dibromomethane	15.6	0.79	2.53	2	0.82	2.61	5
1,2-Dichlorobenzene	25.66	0.82	2.61	2	0.63	2.00	5
1,3-Dichlorobenzene	24.77	0.66	2.11	2	0.58	1.85	5
1,4-Dichlorobenzene	24.95	0.83	2.65	2	0.74	2.37	5
Dichlorodifluoromethane	2.56	0.72	2.28	2	1.03	3.29	5
1,1-Dichloroethane	8.13	1.49	4.75	2	0.94	3.00	5
1,2-Dichloroethane	13.22	0.96	3.07	2	0.66	2.11	5
1,1-Dichloroethene	5.08	0.93	2.95	2	1.38	4.40	5
cis-1,2-Dichloroethene	10.21	0.92	2.93	2	0.80	2.54	5

**Method Detection Limits (MDL), Practical Quantitation Limits (PQL), and
Reporting Limits (RL)**
Method: Volatiles by 8260

Analyte	Ret Times (minutes)	Water (µg/L)			Soil (µg/Kg)		
		MDL	PQL	RL	MDL	PQL	RL
trans-1,2-Dichloroethene	6.81	1.14	3.63	2	0.75	2.39	5
1,2-Dichloropropane	15.33	1.17	3.74	2	0.48	1.54	5
1,3-Dichloropropane	18.98	1.31	4.16	2	0.67	2.12	5
2,2-Dichloropropane	10.01	0.64	2.05	2	1.01	3.23	5
1,1-Dichloropropene	12.25	1.06	3.37	2	0.79	2.51	5
cis-1,3-Dichloropropene	17.03	0.94	2.98	2	0.80	2.55	5
trans-1,3-Dichloropropene	18.3	0.85	2.71	2	0.58	1.83	5
Diisopropyl ether	8.25	1.35	4.31	2	0.87	2.77	5
Ethylbenzene	20.67	0.80	2.53	2	0.79	2.51	5
Hexachlorobutadiene	28.85	(*)	(*)	2	0.81	2.58	5
2-Hexanone	19.17	3.74	11.91	10	3.33	10.61	10
Isopropylbenzene	22.37	0.74	2.35	2	0.60	1.92	5
4-Isopropyltoluene	24.78	0.71	2.26	2	0.67	2.13	5
Methyl Iodide	5.41	0.73	2.34	2	1.57	4.99	5
4-Methyl-2-pentanone	17.44	3.36	10.70	10	2.31	7.37	10
Methyl-t-butyl ether	6.83	1.46	4.65	2	0.94	2.99	5
Methylene chloride	6.27	1.51	4.81	2	1.03	3.26	5
Naphthalene	29.09	(*)	(*)	2	0.91	2.91	5
n-Propylbenzene	23.15	0.66	2.09	2	0.61	1.94	5
Styrene	21.74	1.00	3.20	2	0.53	1.68	5
1,1,1,2-Tetrachloroethane	20.69	0.88	2.80	2	0.96	3.06	5
1,1,2,2-Tetrachloroethane	23.12	1.33	4.24	2	0.69	2.19	5
Tetrachloroethene	18.66	0.57	1.81	2	0.72	2.30	5
Toluene	17.58	0.76	2.41	2	0.68	2.16	5
1,2,3-Trichlorobenzene	29.53	1.16	3.70	2	0.84	2.66	5
1,2,4-Trichlorobenzene	28.64	1.15	3.66	2	0.87	2.78	5
1,1,1-Trichloroethane	11.72	1.18	3.75	2	1.16	3.68	5
1,1,2-Trichloroethane	18.66	0.93	2.97	2	0.57	1.82	5
Trichloroethene	14.66	0.64	2.05	2	0.67	2.12	5
Trichlorofluoromethane	4.12	1.25	3.98	2	1.372	4.37	5
1,2,3-Trichloropropane	23.19	1.43	4.56	2	1.14	3.63	5
1,1,2-Trichloro-1,2,2-Trifluoroethane	5.01	0.89	2.83	2	1.46	4.64	5
1,2,4-Trimethylbenzene	24.21	0.80	2.53	2	0.62	1.99	5
1,3,5-Trimethylbenzene	22.37	0.74	2.35	2	0.58	1.85	5
Vinyl Acetate	8.38	5.62	17.91	10	4.08	12.98	10
Vinyl Chloride	3.01	0.69	2.21	2	1.08	3.45	5
o-Xylene	21.67	0.69	2.19	2	0.63	2.02	5
m,p-Xylene	20.91	1.67	5.31	4	1.33	4.24	10

(*)--The MDL for this compound is currently being reanalyzed.

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

POLYNUCLEAR AROMATIC HYDROCARBONS BY HPLC

GLA 8310 BG

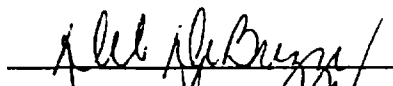

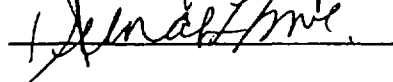
Revision 2.1

Approved By:

Department Manager:

Quality Assurance Manager:

Laboratory Manager:

Date: 5-28-99
Date: 5/23/99
Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of polynuclear aromatic hydrocarbon compounds (PNA's or PAH's) by high performance liquid chromatography (HPLC). This SOP is an interpretation of EPA method 8310. Samples are extracted according to Great Lakes Analytical (GLA) SOP 3500 BG. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for extracts of aqueous, soil/sediment, and non-aqueous solvent-soluble waste samples.

The holding time before extraction for water samples is 7 days and for soil samples 14 days. Samples are stored refrigerated (at ~4°C) prior to extraction - no additional preservation is needed. Sample extracts are stored under refrigeration and analyzed within 40 days of the extraction date.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

This method provides HPLC conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbon (PAH or PNA) compounds:

- 2.1 Samples for PNA analysis are extracted with organic solvents (aqueous samples using separatory funnel liquid-liquid extraction, soil/sediment samples using ultrasonic extraction, GLA SOP 3500 BG, sections 11.1 and 11.3). If the sample matrix is soluble in acetonitrile, a waste dilution may be performed.
- 2.2 Extracts are analyzed by HPLC. Aliquots of the extracts (10 µL) are injected and eluted using an acetonitrile/water gradient on a reverse-phase octadecylsilane column. All compounds, except acenaphthylene, in the effluent are detected by a fluorescence detector - acenaphthylene is detected by an ultraviolet (UV) detector.
- 2.3 Compounds that can be detected by this method include: acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, 1-methyl-naphthalene, 2-methyl-naphthalene, naphthalene, phenanthrene, and pyrene.
- 2.4 The sensitivity of this method is very dependent on the level of interferences rather than instrumental limitations. The limits of detection represent sensitivities that can be achieved in the absence of interferences. When interferences are present, the level of sensitivity will be lower.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest level possible. Gloves are worn when handling solvents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential health hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received into the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for hazardous sample management.

4.0 INTERFERENCES

4.1 GLASSWARE

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interference, under the conditions of the analysis, by running method blanks. Sample extracts can become contaminated if they come in contact with contaminated glassware or syringes used in the extraction and preparation of samples with high concentrations of analytes. Glassware is thoroughly washed, deionized water rinsed, and solvent rinsed as indicated in the glassware preparation SOP. Syringes are rinsed three times with acetone, methylene chloride and acetonitrile before each use. Glassware, syringes, and dilution solvent used in waste dilution extractions are stored separately from routinely used glassware.

4.2 PLASTICS

Phthalate esters contaminate many types of products found in the laboratory. Plastics, in particular, should not be used because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Substantial phthalate contamination may result at any time if consistent quality control is not practiced. Nitrile gloves must be used.

4.3 CO-EXTRACTED INTERFERENCES

Interferences co-extracted from the samples will vary considerably from source to source. The chromatographic conditions described allow for a unique resolution of the specific PNA/PAH compounds covered by this SOP. Other compounds, in addition to matrix artifacts, may interfere. An oily matrix will have an effect on the sensitivity of the procedure as well. Oily samples are typically diluted.

4.4 CARRYOVER

Contamination by carryover can occur whenever samples with high concentration and low concentration are analyzed sequentially. The sample syringe may be rinsed out between samples with water or solvent to reduce carryover. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or water to check for cross contamination.

5.0 RECORD KEEPING

5.1 INSTRUMENT LOG

For each HPLC instrument, an instrument maintenance logbook is kept. It contains the instrument name, beginning date and ending date of the Logbook on the front cover. This book will include all routine instrument maintenance, repairs and any instrument modifications. All entries must be dated and initialed.

5.2 QUALITY CONTROL BOOK

A Quality Control Book is set up for each method. It has the method identification number on the outside cover. This contents of each book include:

- Copy of the GLA Quality Assurance Program manual.
- Copies of the GLA SOP and source methods.
- Copies of all calibration data.
- Copies of all method detection limit studies and dates in use.
- Copies of all retention time studies and dates in use.
- Copies of accuracy and precision studies.
- Copies of all control limit studies.
- Surrogate standard recovery tabulations and control limits.

5.3 RUN LOG

The front cover of the Run Log notebook displays:

- Instrument identification number.
- Method number.
- Run log number.
- Effective dates.

In the front of the notebook record:

- Calculations represented with a generic calculation.
- The names and concentrations of the internal standard and surrogate standard(s).

The following column headings are written at the top of each page, and may include:

- Data file name.
- Dates of extraction and analysis.
- Autosampler position.
- Client.
- Full sample number.
- Amount of sample used - dilution, if any.
- Comments.

Subsequent information for each sample and standard is then documented under the column headings. Additional documentation concerning standards includes:

- Quality control function (check standard, blank, matrix spike, etc.)
- Concentration.
- GLA code number.
- Recovery.

Each page is dated and signed. Laboratory notebooks must be neat and legible. Mistakes and crossed out with a single line, initialed, and dated. Unused or partial pages are z'ed out.

5.4 STANDARD PREPARATION LOG

When standards are received by the laboratory, the certificate of analysis is dated and placed in the Standards Preparation Certificate of Analysis binder. A log is kept of all standards prepared for the method. Document in the book:

- Analyte, purpose (method, calibration, internal, etc.).
- Supplier.
- Lot number.
- Initial concentration of the stock solution.
- Expiration date of stock standard - 3 months after the standard has been opened, or the date set by manufacturer, whichever is first.
- Initials and date.

Also for working standards:

- Volume diluted.
- Volume prepared.
- Final concentration.
- Expiration of working standard - 6 months after the standard has been prepared, or when the standard fails Quality Control criteria, whichever is first.
- GLA code(s) for the final solution(s). The GLA code is an alphanumeric sequence used to track standard preparations within the lab in a method-type-date-(letter) format. For example, "8270 CAL 020599 A" indicates method 8270, calibration standard, prepared 2/5/99, first concentration level (A).

6.0 QUALITY CONTROL

6.1 METHOD BLANKS AND SAMPLE SPIKES

For quality control, each water extraction batch contains a method blank (MB), and a blank spike (BS), and a blank spike duplicate (BSD). (An analytical batch does not contain more than 20 samples.) Deionized water is used for water method blanks and spikes.

Each soil extraction batch contains a method blank (MB), a lab control spike (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). Clean sand is used for soil method blanks (MB) and spiked blanks (LCS). Samples selected randomly by the LIMS are used for matrix spikes and matrix spike duplicates.

A surrogate compound is added to all samples, blanks, and spikes in an analytical batch.

6.2 CHECK STANDARD

Each day before analysis of samples begins, the calibration curve is verified using a check standard. (This standard is from a different source/vendor than the calibration standard.) The check standard is run and quantitated every 12 hours, or every 20 samples, whichever is more frequent. The chromatography of the check standard is evaluated for peak shape and co-elution problems. Each day, a successful Check Standard must be analyzed before sample analyses can begin. A successful check standard contains all analytes with 85-115% recovery. Corrective action must be taken for those analytes that fall outside these limits.

6.3 METHOD BLANK

No contaminants should be present in the blank above the method detection limit. If contaminants are found the blank and all related samples must be reanalyzed. If the blank contamination persists, the samples are re-extracted. A blank is extracted with every batch.

6.4 SURROGATE STANDARD

Surrogate standards are used to monitor the efficiency of the procedure. The surrogate standard for this method is 7,12-dimethylbenz(a)anthracene. The control limits for the surrogate are calculated as the average percent recovery plus/minus 3 standard deviations. Surrogate standard limits are kept in the QC binder and should be posted by the analyst for reference.

6.5 MATRIX SPIKES

A blank spike and blank spike duplicates are analyzed with all samples. Spikes are run every 10 samples. Spike recoveries for all compounds are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery per matrix for a particular compound plus/minus 3 times the standard deviation.

6.6 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken to document steps taken to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- Recovery for check standard fails.
- Contamination was present in the blank and in the sample.
- Recovery for the laboratory control sample outside of limits.

6.7 CONFIRMATION

The ultraviolet (UV) detector is used to confirm the presence of PNA/PAH's. GC/MS may be used for the confirmation of moderate to high levels of PNA/PAH's.

6.8 DATA REVIEW

Data obtained by this method are reviewed by another analyst or a supervisor to ensure accuracy of results. (See Data Review Checklist attached to this SOP.)

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory. Extraction Logbooks contain records of sample extractions and preparations for analytical batches.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for method 8310 are queued under "EXTR" and "HPLC". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 CALIBRATION STUDY

A calibration study determines the response factors (RFs) for analytes that are used for the determination of concentrations of analytes in samples. A series of different concentrations of analytes is compared to respective peak area responses on a chromatogram. A minimum of 5 concentration levels is required (see Section 10.1.2).

A response factors (RF) is calculated by tabulating responses of each analyte against the known concentrations of the analytes. The curve is considered linear and an average RF may be used if the relative standard deviation (%RSD) is less than 20%. If the %RSD for any compound is greater than 20%, linear regression is used to establish the equation of the calibration curve for that particular compound: $\text{peak area} = \text{slope} \times \text{concentration} + \text{constant}$. Linear regression is valid only if the correlation coefficient (r^2) is 0.99 or greater.

Procedure summary:

- Prepare and analyze a minimum of 5 concentration levels that span the linear range of the system with the lowest level near, but above, the MDL. (Surrogate standard is added at the same level as other compounds.)
- For each compound, calculate:
 - *
$$RF = \frac{\text{peak area of analyte}}{\text{concentration of analyte}}$$
 - * Average and standard deviation for RFs
 - *
$$\%RSD = \frac{\text{standard deviation of RFs}}{\text{average RF}} \times 100$$
- If the %RSD is less than 20%, the average RF value is used.
- If the %RSD is greater than 20%, a calibration curve is generated using linear regression.
- The correlation coefficient for the linear regression must be 0.99 or greater.
- Check standards are analyzed following a calibration study.
- Recovery for the check standards must be between 85 and 115%.

8.2 DETECTION LIMIT STUDY

This study is performed in accordance with the GLA Quality Assurance Program. This study provides the analyst with the minimum detection limit (MDL) for the instrument and analytes. The MDL is defined as the minimum concentration of the analyte that can be measured and reported at a 99% confidence level. The MDL is equal to the standard deviation of the recoveries of 7 aliquots times the t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The t value appropriate for 7 aliquots is 3.143. The calculated MDL must be between 10% and 100% of the concentration of the MDL standard in order for the study to be valid. For example, if you inject 1 µg/L of standard, the calculated MDL must be between 0.1 and 1 µg/L. A MDL study is done yearly.

Procedure summary:

- Analyze 7 replicates of low level standard (at or below lowest calibration level standard).
- Calculate standard deviation for the 7 replicates.
- $\text{MDL} = \text{standard deviation} \times 3.143$.
- The calculated MDL must be less than the reporting limit.

8.3 RETENTION TIME WINDOW STUDY

The retention time window study is used as a guide for the tentative identification of peaks during sample analyses. A retention time window study is performed annually, by new analysts, or when a new column is installed.

Procedure summary:

- Analyze the check standard 3 times over a 3 day (72 hour) period.
- Calculate the average retention time and associated standard deviation for each compound.
- For each compound, retention time window = average retention time $\pm 3 \times$ standard deviation. (A standard deviation of 0.01 may be used if the calculated standard deviation is less than 0.01 minutes)
- If the instrument is equipped with Enviroquant, enter the retention time windows into the initial calibration tables.

8.4 ACCURACY AND PRECISION STUDY

Each new analyst will perform a series of analyses to establish the ability to generate acceptable precision and accuracy (demonstration of proficiency).

Procedure summary:

- Analyze 4 replicate standards or spiked extracts for both water and soil matrices.
- Recoveries of each compound must be between 80 and 120%.
- The %RSD of each set must be less than 20%.

9.0 EQUIPMENT

9.1 High performance liquid chromatograph (HPLC), consisting of:

- Pumping system - capable of gradient chromatography - Waters 510, Hewlett-Packard 1050, or equivalent.
- Sample injector/controller - Waters WISP 712, Hewlett-Packard 1050, or equivalent.
- Analytical column - reverse-phase HC-ODS Sil-X, 5 μ particle size, 25 cm \times 2.6 mm ID, or VYDAC C-18, 5 μ particle size, 25 cm \times 4.6 mm ID (Perkin Elmer no. 089-0716, or equivalent).
- Ultraviolet (UV) detector - capable of detection at 254-nm - Waters 486, Hewlett-Packard 1050, or equivalent.
- Fluorescence detector - for excitation at 280 nm and emission greater than 389 nm - Waters 470, Hewlett-Packard 1046A, or equivalent.
- Data collection and analysis system.

9.2 Glass syringes, various sizes.

9.3 Volumetric flasks, various sizes.

10.0 STANDARDS AND REAGENTS

10.1 STANDARD SOLUTIONS

10.1.1 Stock Standard Solutions:

- a. Commercially prepared stock standards are purchased from various suppliers. Standards can be ordered from EPA or A2LA certified companies. These companies include AccuStandard, Restek, Supelco, and Ultra Scientific. Two different sets of standards are used for this analysis. One set of standards is used for instrument calibration, and contain the PNA/PAHs at several concentrations. The other set of standards is used for spiking of blanks (BS/BSD) and samples (MS/MSD), and has all analytes at the same concentration levels. In addition, the second set of standards is used for the preparation of the daily check standard.

- b. The stock standards are transferred into Teflon-sealed screw-cap vials. The standards are stored refrigerated (at -4°C) and protected from light. Stock standards are checked for signs of degradation or evaporation.
- c. Stock standard solutions are replaced after one year, or sooner if comparison with check standard indicates a problem.

10.1.2 Calibration Standards:

- a. Calibration standards at a minimum of five concentration levels are prepared through dilution of the stock standards with acetonitrile. One of the standards is at a concentration near, but above, the instrument detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the HPLC. Due to the varying response of the target compounds, more than five points are analyzed. The initial calibration consists of standards at 5.0, 10, 50, 100, 500, 1000, 2000, 3000, 5000, 7000, and 10000 ng/ml. The calibration stock standard must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.
- b. Calibration standards are made up of 4 ampules which are combined to contain all 18 target compounds and the surrogate. The first ampule contains a PNA mix that contains all (16) target compounds except the surrogate 7,12-dimethylbenz(a)anthracene, 1-methylnaphthalene, and 2-methyl-naphthalene. The other 3 ampules are for each of the three remaining compounds (AccuStandard no's. 4-8743, 4-0567, 4-8162, and 4-8366).

The typical concentrations found in the ampules are:

PNA (PAH) Mix	2000 $\mu\text{g/mL}$
7,12-Dimethylbenz(a)anthracene	1000 $\mu\text{g/mL}$
1-Methylnaphthalene	1000 $\mu\text{g/mL}$
2-Methylnaphthalene	1000 $\mu\text{g/mL}$

Prepare a 50-mL aliquot of 10,000 $\mu\text{g/L}$ solution by adding 500 μL of 7,12-dimethylbenz(a)anthracene, 1-methylnaphthalene and 2-methylnaphthalene. Add 250 μL of the PNA mix and bring up to volume with acetonitrile. Use this 10,000 $\mu\text{g/L}$ stock solution to prepare a set of standards which range from 5.0 ppb to 7,000 ppb and using the 10,000 ppb stock solution as the final standard.

- 10.1.3 Surrogate Standards: This analysis is monitored for the performance of the extraction, cleanup (if necessary), analytical system, and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with a surrogate compound. 7,12-Dimethylbenz(a)anthracene is used as the surrogate (AccuStandard no. 4-0567 or Restek no. 31286), at a concentration of 100 $\mu\text{g/mL}$.
- 10.1.4 Spike Standards: Restek SV CAL Mix #5 (no. 31011, 16 PNA/PAH compounds), 1-methylnaphthalene (Restek no. 31283), and 2-methylnaphthalene (Restek no. 31285), at a concentration of 100 $\mu\text{g/mL}$.

10.2 STANDARD DILUTIONS

A useful equation for preparations of diluted standards is:

$$C_2 \times V_2 = C_1 \times V_1$$

C_1 = concentration of the stock standard.

C_2 = desired or calculated concentration of the working standard.

V_1 = volume of the stock standard diluted.

V_2 = volume of working standard prepared.

10.3 STOCK STANDARD

Transfer stock standard to a vial and seal with a Teflon-lined cap. Label this vial with:

- Analyte description.
- Manufacturer.
- Lot number.
- Concentration.
- Date opened.
- Expiration date.

Opening of the standard is documented in the Standard Log.

10.4 WORKING STANDARD

Standards are prepared in acetonitrile:

- Determine volumes of stock and working standard required.
- Fill volumetric flask about $\frac{3}{4}$ full with solvent.
- Add required volume of stock standard.
- Fill volumetric to the mark.
- Cap and invert three times.
- Transfer to amber vials with Teflon caps.
- Label vial with:
 - Analyte description.
 - Concentration of standard.
 - Date prepared.
 - Purpose (method).
 - Initials.
 - Expiration date.
 - GLA code.

Preparations are documented in the Standard Log.

NOTE: A $5\mu\text{L}$ aliquot of a $10\text{ ng}/\mu\text{L}$ working standard is equivalent to 50 ng :
 $10\text{ ng}/\mu\text{L} \times 5\mu\text{L} = 50\text{ ng}$

The GLA code is an alphanumeric sequence used to track standard preparations within the lab in a method-type-date-(letter) format. For example, "8270 CAL 020599 A" indicates method 8270, calibration standard, prepared 2/5/99, first concentration level (A).

10.5 REAGENTS

- 10.5.1 Reagent water - water in which an interference is not observed at the method detection limit of the compounds of interest (PNA/PAHs).
- 10.5.2 Acetonitrile - HPLC grade, or equivalent.
- 10.5.3 Helium - ultra-high purity grade, for sparging mobile phases.
- 10.5.4 Compressed air or nitrogen - for operation of pneumatic instrumentation/equipment.

11.0 PROCEDURE

NOTE: Method Validation (section 8.0) must be completed before samples can be analyzed. Samples are analyzed in the same manner as method validation solutions. Appendix A contains example chromatograms for this method.

- 11.1 HPLC Gradient Programs: The solvent gradient program used for the analysis of PNAs are as follows:

Waters Systems

Flow Rate: 2.0 ml/min.

Gradient:

<u>Time (minutes)</u>		<u>% Acetonitrile</u>	<u>% Water</u>
Initial		50	50
3.0		50	50
9.0	linear to	60	40
17.0	linear to	75	25
27.0	linear to	90	10
28.0	linear to	91	9
29.0	linear to	50	50
45		50	50

Hewlett Packard System:

Flow Rate: 1.25 ml/min

Gradient:

<u>Time</u>		<u>% Acetonitrile</u>	<u>% Water</u>
Initial		50	50
5.0		50	50
10.0	linear to	60	40
17.0	linear to	75	25
27.0	linear to	90	10
28.0	linear to	91	9
35.0	linear to	100	0
35.1	linear to	50	50
40.0		50	50

- 11.2 The analyst plans the sequence, enters the sample numbers into the sequence file, and records all the needed information into the Run Log. The daily sequence will be as follows:

- A. Check standard (contains all compounds with each RF \leq 15% difference from initial calibration).
- B. Acetonitrile blank.
- C. Samples or QC samples (number of samples/QC based on 12 hour clock).
- D. Check standard.
- E. Repeat steps C and D.

- 11.3 The chromatography of the check standard is evaluated for peak shape and co-elution problems. The calibration check standard is quantitated and all QC criteria must be met before analysis of samples can begin. All reportable samples and spikes must be bracketed by valid check standards. Any samples not bracketed must be reanalyzed.

- 11.4 HPLC analysis - the sequence of steps necessary to clean, equilibrate, and perform instrumental analysis follows:

11.4.1 Daily Maintenance:

- Check helium tank pressure.
- Check compressed air tank pressure.
- Fill acetonitrile reservoir.
- Fill water reservoir.
- De-gas newly filled solvents for approximately 15 minutes.
- Fill needle wash bottles with acetonitrile.
- Dispose of solvent waste in flammable solvent waste drums.
- Remove check standard and all samples to be run from the refrigerator and allow to come to room temperature.

11.4.2 Analyze samples:

- a. Operate gradient function - necessary to prepare the instrument for the initial conditions to run the samples:
 - On the Gradient controller, press [OPERATE GRADIENT] [8] [ENTER] [ENTER] [2] [ENTER].
 - The instrument should run without sample injection at this setting for approximately 5 minutes.

A typical gradient profile used is 50% acetonitrile initially for 5 minutes, linear gradient to 100% acetonitrile over 25 minutes, with a mobile phase linear velocity of 2 mm/sec (e.g. 1.5 mL/min for a 4.6 mm ID column).

- b. Create the sequence - necessary to collect and retrieve data from samples that have been run - in the GCTop:
 - Select [SEQUENCE-SAVE].
 - Enter the date you want the data saved under.
 - Select [EDIT SEQUENCE LOG].
 - Enter the amount of samples that will run with the appropriate method and individual sample information. Select [MORE] to enter additional information such as sample dilutions and printing options (select "NONE" as a printing option so the sample information will not print during the run). When all information has been entered choose [OK].
 - Select [LOAD AND RUN SEQUENCE].
 - Choose [OK] at the prompts, choose and enter correct date.
 - When prompt reads "READY TO INJECT", run can begin.
- c. Starting the run on the WISP - this will inject the samples and begin the run:
 - Open the door and place samples in the carousel.
 - While door is still open press [SYS MES] [7] [7] [ENTER], then the last sample number in the carousel, [ENTER].
 - Close the door, press [RUN/STOP], the red light will move from STOP to RUN.
 - To pause WISP during a run, open door - this will prevent the next sample from being injected.

11.4.3 Generate reports - reports consist of sample results and corresponding chromatograms:

- a. Load data file - bring up the file to be quantitated. The samples run on LC-1 will be found in "c:\hpchem\5\data\date" run. The samples run on LC-2 will be found in "c:\hpchem\6\data\date" run.
- b. Update retention times - Update the retention time of the first check standard run before that sample. To do this select [TOOLS] [EASYID], underline each peak for the appropriate compound. After updating and saving all peak changes, choose [FILE] [SAVE METHOD] to save to the method. Quantitate all samples run after the check standard with that check standards retention times. When subsequent check standard appears, repeat the above procedure.

- c. Quantitate results - After updating the proper check standard retention times, pull up the sample file you wish to quantitate. Be sure the correct method is loaded and then choose [CALCULATE AND GENERATE REPORT]. If any compounds required manual integration, select [QUANT] [Q EDIT QUANT RESULT]. Every attempt should be made to avoid the use of manual integration. If absolutely necessary, it must be performed in a manner which is consistent with the integration of the standards used for calibration. The manipulation of integration parameters in a way that is inconsistent with the integration of the calibration standards constitutes fraud, and is strictly forbidden.
- d. Print results - To print results that have been quantitated, select [TOOLS] [DO LIST] [SUMMARY QUANT W/OUT CALCULATIONS], and highlight those to be printed. This will print the quantitated results with any Qedit changes made.

11.4.4 Calculations - Divide by factors necessary to convert report results (instrument report values in ppb) to reportable units. These calculations assume a starting volume of 1 L of sample for waters and 30 g of sample for soil samples.

Waters in ug/L:	Result / 100
Illinois Soils in ug/kg:	Result / 3
Wisconsin Soils in ug/kg :	Result / 3 x Dry Weight

If the sample volume or weight is less than the assumed starting value, then a dilution factor is applied to the above calculations.

11.5 QC Calculations:

11.5.1 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.5.2 Relative Percent Difference (%RPD) for duplicate analyses:

$$\% \text{RPD} = \frac{|\text{Conc. of 1}^{\text{st}} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of 1}^{\text{st}} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

11.6 If all the QC requirements for the day have been met, the samples have been analyzed at the proper dilution, and analytes found in the samples (hits) have been confirmed, the results are ready for peer review.

11.7 Reporting Results - Once analysis is completed for a group of samples and all QC measures have been satisfied, sample results can be recorded on the report worksheets. The analyst records the date of analysis for the sample. When recording the results on the worksheet the analyst circles the compound with a positive result, and the ND is crossed out. Next to the ND, the concentration found in the sample is recorded. After an analyst has recorded the results for each sample he/she signs, and dates the first reporting page for that analysis. The analyst also records results of the spike and spike duplicate data on the QC sheet attached to the report.

11.8 LIMS Reporting - All sample results should be downloaded into the LIMS on a regular basis.

11.8.1 Batching - must be done before results can be transferred to LIMS. There are several ways to batch samples. One way is to clone the extraction batch so that the analysis batch corresponds to the extraction batch:

[BATCHES] - [EDIT] - [BY BATCH] - F8

Queue = type HPLC (all caps)
Batch Rule = press [F2] , enter
Batch Queue = type EXTR (all caps)
Batch = the numerical extraction batch that is being cloned.

Press [F4] twice, the extraction batch will now be given an HPLC batch number as well and the samples are ready to be transferred (posted) to LIMS.

11.8.2 Do List - done in Enviroquant, this is the process of converting the data files collected to .CSV files in the C drive. This can only be done after the samples results have been batched:

select [TOOLS]
[DO LIST]
[QUANT TO FORMS W/O CALC] [OK]
Highlight the samples to be transfered and choose [ADD] [PROCESS].

In order for the samples to be converted, the correct format must be used when entering sample information in the sequence including any dilution factors used. The following are examples for method 8310 water, soil, SPLP, and method 610:

GLA sample #|HPLC|8310WA|OK
GLA sample #|HPLC|8310SA|OK
GLA sample #|HPLC|8310PA|OK
GLA sample#|HPLC|610|OK.

11.8.3 Posting - transferring the .CSV files from the C drive to the LIMS drive. Can only be done at the Department Manager's terminal:

From FILE MANAGER, the files will be in C:\posted. Copy the files contained in "posted" to the HPLC LIMS drive. After the copies have been made, the files in "posted" can then be deleted.

11.8.4 Parsing - done in LIMS to process the .CSV files sent by POSTING.

select [SYSTEM] [PARSERS]
Program = press [F2] and chose HPCHEMST
Action = type START (all caps)
Cycle = type [1]
Press [F4] to commit and [ENTER] at the prompt.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be used who may be unsure of the instrumentation and a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 ISOLATE THE PROBLEM

When troubleshooting the system for a chromatography or sensitivity problem, it is important to change only one thing at a time. A standard should be run after every change to see if any progress has been made.

Some troubleshooting suggestions (problem - possible remedy):

- Broad peaks or poor peak resolution - change guard column.
- High pressure - change guard column.
- No or low pressure - prime pump, check for leaks.
- Noisy baseline - check source.
- No peaks - check the gradient program.
- Increased retention times - flow rate decreasing, check for leaks.
- Upon opening door of WISP tray will not release - check air tank.

13.0 REFERENCES

- 13.1 Testing Methods for the Evaluating of Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Methods 3510B, 3550B, 8000B, and 8310.
- 13.2 Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters, EPA-600/4-82-025, US. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 (September 1982).
- 13.3 EPA Method Validation Study 20, Method 610 (Polynuclear Aromatic Hydrocarbons), Report for EPA Contract 68-03-2624.
- 13.4 EPA 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule (October 26, 1984).
- 13.5 Interpretation of Percent Recovery Data, L.P. Provost and R.S. Elder, American Laboratory, vol. 15, pp. 58-63 (1983).
- 13.6 Great Lakes Analytical Quality Assurance Program manual.
- 13.7 Great Lakes Analytical Chemical Hygiene Plan.
- 13.8 Great Lakes Analytical SOP for Login Department.
- 13.9 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to the Great Lakes Analytical Quality Assurance Program Manual.

APPENDIX A.

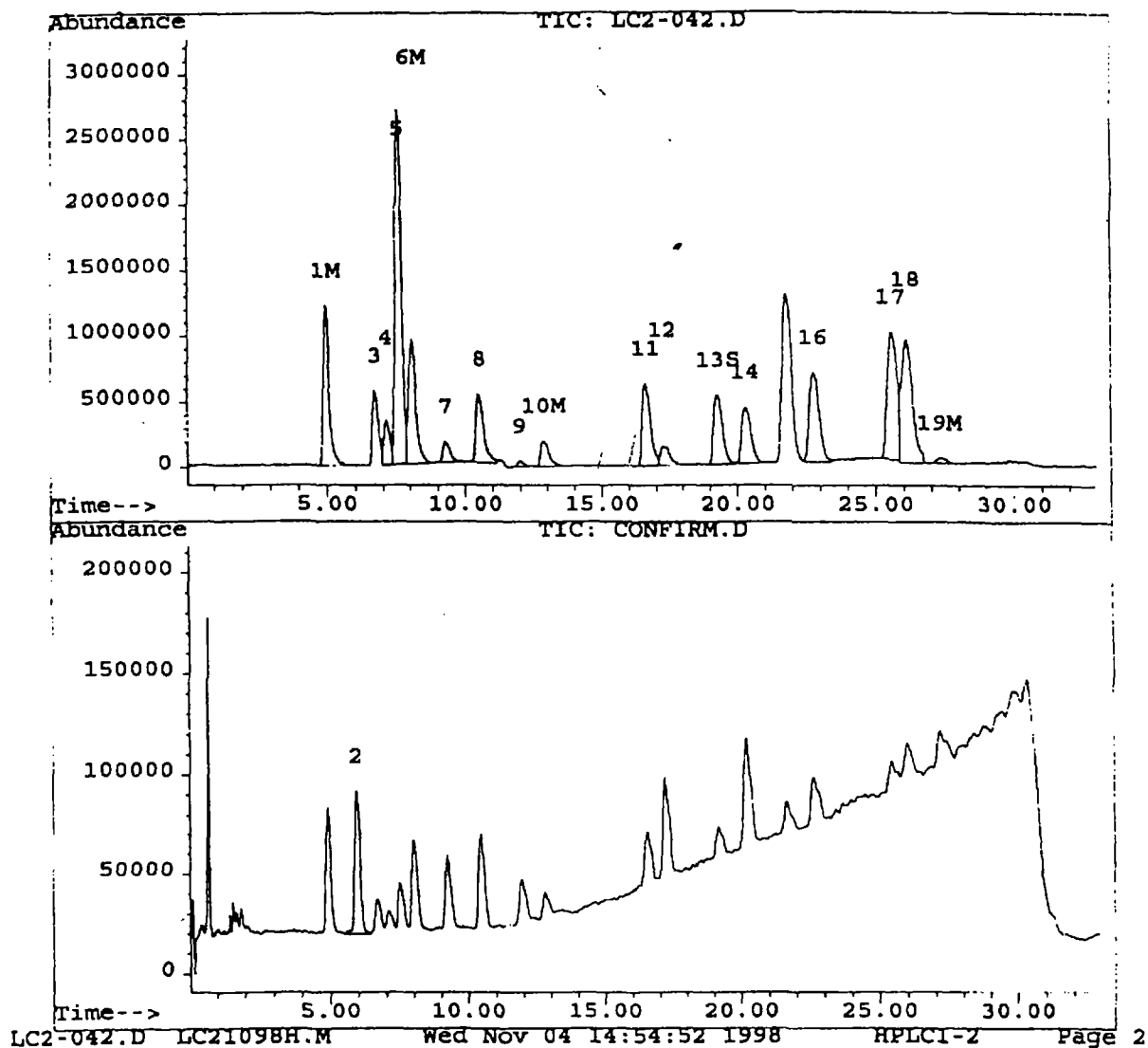
EXAMPLE CHROMATOGRAMS.

<u>Peak No.</u>	<u>Compound</u>	<u>Approximate R.T. (min)</u>	<u>Typical Response, Fluorescence (area counts $\times 10^6$)</u>
1	Naphthalene	4.9	17.8
2	Acenaphthalene	5.9	1.0†
3	1-Methylnaphthalene	6.7	8.9
4	2-Methylnaphthalene	7.1	5.2
5	Acenaphthene	7.5	43.7
6	Fluorene	8.0	16.9
7	Phenanthrene	9.3	2.8
8	Anthracene	10.5	10.5
9	Fluoroanthene	12.0	0.8
10	Pyrene	12.9	4.5
11	Benzo(a)anthracene	16.6	13.3
12	Chrysene	17.2	3.5
13	7,12-Dimethylbenz(a)anthracene	19.3	11.9
14	Benzo(b)fluoranthene	20.3	10.0
15	Benzo(k)fluoranthene	21.7	<0.1
16	Benzo(a)pyrene	22.7	17.2
17	Dibenzo(a,h)anthracene	25.5	22.7
18	Benzo(g,h,i)perylene	26.1	25.8
19	Indo(1,2,3-cd)pyrene	27.3	1.0

† Ultraviolet (UV) detector response.

Top chromatogram: Fluorescence detector

Bottom chromatogram: Ultraviolet detector



DATA REVIEW

		YES	NO	CA	FLAG
1	Check standard recoveries within $\pm 15\%$?				
(8081) 1b	Prime and blank run?				
(8081) 1c	Endrine DDT breakdown < 15 % ?				
(8270) 1d	DFTPP tune evaluated and passing?				
(8270) 1e	SPCC average response factor > 0.050 ?				
(8270) 1f	CCC % deviation > 20 % ?				
(8270) 1g	Internal recoveries within 50-100 % ?				
2	Method blank recoveries < reporting limits?				
3	LCS within control limits?				
4	MS/MSD within control limits?				
5	All surrogate recoveries within control limits?				
6	All hits out of cal range diluted and re-analyzed?				
7	All sample holding times met?				
8	No transcription errors?				
9	No calculation errors?				

COMMENTS:

Analyst review signature: _____

Date: _____

**Method Detection Limits (MDL), Practical Quantitation Limits (PQL), and
Reporting Limits (RL)**

Method: PNAs by 8310

Analyte	Water (µg/L)			Soil (µg/Kg)		
	MDL	PQL	RL	MDL	PQL	RL
Naphthalene	0.017	0.060	3	0.87	3.08	30
Acenaphthylene	0.582	2.065	4	91.34	323.62	200
Acenaphthene	0.028	0.099	5	6.85	24.28	30
Fluorene	0.029	0.104	1	0.91	3.24	30
Phenanthrene	0.037	0.130	0.3	1.62	5.73	30
Anthracene	0.019	0.069	0.2	0.40	1.28	30
Fluoranthene	0.016	0.057	1	4.76	16.88	30
Pyrene	0.009	0.032	1	4.32	15.32	30
Benzo (a) Anthracene	0.038	0.136	0.1	0.48	1.69	30
Chrysene	0.020	0.070	0.05	1.55	5.50	30
Benzo (b) Fluoranthene	0.010	0.033	0.02	0.38	1.21	30
Benzo (k) Fluoranthene	0.010	0.037	0.05	0.85	3.02	30
Benzo (a) Pyrene	0.023	0.081	0.05	0.67	2.38	30
Dibenzo (a,h) Anthracene	0.019	0.059	0.02	0.88	3.13	30
Benzo (g,h,i) Perylene	0.020	0.069	0.06	0.94	3.32	30
Indeno (1,2,3-cd) Pyrene	0.017	0.061	0.2	4.53	16.06	30

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

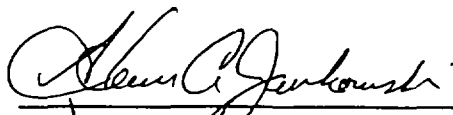
THE DETERMINATION OF pH

GLA 9040 BG

Revision 2.0

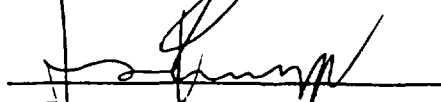
Approved By:

Department Manager:



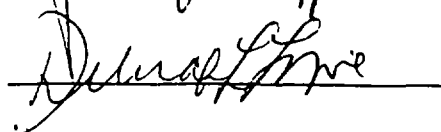
Date: 5/27/99

Quality Assurance Manager:



Date: 5/27/99

Laboratory Director:



Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of aqueous and solid samples for pH. This SOP is an interpretation of SW-846 methods 9040B, 9041, and 9045C, and Standard Methods no. 4500-H⁺. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to aqueous wastes and multiphasic wastes where the aqueous phase constitutes at least 20% of the total volume of the sample. In addition, samples may be solids, sludges, or non-aqueous liquids, with water less than 20% of the total volume. Samples should be analyzed as soon as practical.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

The pH values of samples are determined electrometrically using either a glass electrode in combination with a reference potential, or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH. Aqueous samples are analyzed directly, solid samples are mixed with water and the pH of the aqueous portion determined. Alternatively, samples which might damage or seriously coat the electrode (ex., oils) are prepared appropriately and the pH is determined by a pH-sensitive paper.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

4.0 INTERFERENCES

- 4.1 Glass electrodes are generally not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate (< 0.1 M) salinity.

- 4.2 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, or sonication, followed by rinsing with distilled water. An additional treatment with 10% hydrochloric acid may be necessary to remove any remaining film.
- 4.3 Samples with very low or very high pH may give incorrect readings on the meter. Strongly basic solutions, with a true pH >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strongly acidic solutions, with a true pH <1, may give incorrectly high pH measurements.
- 4.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference is controlled with instruments with temperature compensation or by calibrating the system at the temperature of the samples. The second source of temperature effects is the change in pH due to changes in the sample as the temperature changes. This error is sample dependent and cannot be controlled. It should be noted by reporting both the pH and temperature at the time of analysis.
- 4.5 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in reagent and sample preparations. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with water. Periodic cleaning of sample preparation and analysis areas, including replacement of severely contaminated benchtop covers, will be performed.

5.0 RECORD KEEPING

- 5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed, as well as daily checks of the conductance meter and reagent water supplies.

5.2 pH Log Book:

A log book will be maintained for all pH determinations. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- | | |
|---|---------------------------------|
| • Method reference number | • Sample temperatures |
| • Client Name for each set of samples | • Check standard identifier |
| • GLA Sample I.D. (one complete for each set) | • LIMS batch reference number |
| • Analyst's signature and date | • Reviewer's signature and date |

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out. Daily water supply monitoring results are recorded in a separate book.

- 5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 Meter Calibration Verification

The pH meter is calibrated each day of use (see Section 11.1). After the calibration is performed, it is verified upon each use during the course of the day. A 7.0 calibration buffer solution is read, and must be 95 to 105% of 7.0. If this is not obtained, the meter is recalibrated using fresh buffer solutions.

6.2 Check Standard

A 7.0 calibration buffer solution is read before any sample pH readings are taken, and the reading must be 7.0 ± 0.1 pH units. This check standard is analyzed at the beginning and end of each set of 20 or less samples. If the check standard does not meet the acceptance criteria, the meter is recalibrated and the effected samples are reanalyzed.

6.3 Duplicate Samples

With each set of 20 or less samples per matrix, a sample is analyzed in duplicate. A $\pm 10\%$ relative percent difference (RPD) is used as a guideline for replicate readings. If the duplicate analysis does not meet this criteria, corrective action must occur, which may include reanalysis of the samples or qualifying the effected sample results.

6.4 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.5 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result out of control.
- A deviation from the normal SOP for the method is discovered, and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "WETC". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in a QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Corrective action sheets.

8.2 Quality Assurance Program

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Plan.)

9.0 EQUIPMENT

- 9.1 pH meter and probe - glass electrode with reference, or combination probe, Fisher Accumet 25, or equivalent.
- 9.2 Magnetic stirrer and Teflon-coated stir bars.
- 9.3 Beakers, 250-mL size.
- 9.4 Thermometer, minimum calibrated range of 10-30°C.
- 9.5 Analytical balance, capable of weighing to the nearest 0.1 g.

10.0 STANDARDS AND REAGENTS

- 10.1 ASTM Type II reagent water (DI water).
- 10.2 Standard buffer solutions - commercially available solutions that have been validated by comparison to NIST standards; examples, Fisher no. SB101 (pH 4), no. SB107 (pH 7), and no. SB115 (pH 10).

11.0 PROCEDURE

11.1 CALIBRATION

The instrument/electrode system is calibrated with a minimum of two buffer solutions that bracket the expected pH values of the samples, and are approximately 3 pH units apart. The pHs of the calibration buffer solutions are 4.0, 7.0, and 10.0. Adjustments are made until readings of the buffer solutions are within 0.05 pH units of expected values. This calibration is performed daily when samples are analyzed.

NOTE: If an accurate pH reading based on the conventional pH scale of 0 to 14 at 25°C is required, the analyst should control sample temperature at 25±1°C when sample pH approaches the alkaline end of the scale (pH ≥ 11).

11.2 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

- 11.2.1 Liquids - Aliquot 50 to 100 mL of sample into a clean 250-mL beaker, and add a clean magnetic stir bar. Prepare one sample, per twenty or less, in duplicate.
- 11.2.2 Soils/Solids - Weigh 20 to 50 g of sample into a clean 250-mL disposable beaker, and add an equal amount of reagent water and a clean magnetic stir bar. Mix thoroughly for five minutes, and allow to settle for about 60 minutes. Prepare one sample, per twenty or less, in duplicate.
- 11.2.3 Non-aqueous liquids/Wastes - Aliquot 20 to 50 g of sample into a clean 250ml disposable beaker and add an equal amount of reagent water and a clean magnetic stir bar. Mix thoroughly for five minutes, and allow to settle for about 15 minutes. Prepare one sample, per twenty or less, in duplicate.